PB85-173714

Chemical Transformation Modules for Eulerian Acid Deposition Models
Volume 1. The Gas-Phase Chemistry

National Center for Atmospheric Research
Boulder, CO

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Feb 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-173714

EPA/600/3-85/015
February 1985

CHEMICAL TRANSFORMATION MODULES FOR EULERIAN ACID DEPOSITION MODELS

Volume I. The Gas-Phase Chemistry

by

J. Alistair Kerr and Jack G. Calvert

National Center for Atmospheric Research
Box 3000, Boulder, Colorado 80307

Interagency Agreement DW 930237

Project Officer

Marcia C. Dodge

Atmospheric Chemistry and Physics Division
Atmospheric Sciences Research Laboratory
Research Triangle Park, NC 27711

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

PB85 173714 /AS

1. REPORT NO.
EPA/600/3-85/015

2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE
CHEMICAL TRANSFORMATION MODULES FOR EULERIAN
ACID DEPOSITION MODELS
Volume I. The Gas-Phase Chemistry

5. REPORT DATE
February 1985

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J. A. Kerr and J. G. Calvert

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
National Center for Atmospheric Research
Box 3000
Boulder, Colorado 80307

10. PROGRAM ELEMENT NO.
CCVN1A/02-3195 (FY-85)

11. CONTRACT/GRANT NO.
Interagency Agreement DW93023

12. SPONSORING AGENCY NAME AND ADDRESS
Atmospheric Sciences Research Laboratory-RTP,NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

13. TYPE OF REPORT AND PERIOD COVERED
Interim (8/83-7/84)

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This study focuses on the review and evaluation of mechanistic and kinetic data for the gas-phase reactions that lead to the production of acidic substances in the environment. A master mechanism is designed that treats oxides, sulfur dioxide, ozone, hydrogen peroxide, ammonia, the simple amines (methyl, dimethyl, trimethyl, and ethyl amines), chlorine, hydrogen sulfide, dimethyl sulfide, the hydrocarbons (methane, ethane, propane, butane, 2,3-dimethylbutane, the C_5-C_8 alkanes, ethylene, propylene, trans-2-butene, isobutene, benzene, toluene, m-xylene, isoprene, alpha-pinene), and the variety of oxidation products of these species including the transient free radicals, aldehydes, ketones, hydroperoxides and other molecules. The reaction mechanisms and the rate constants for certain of the chemical transformations are identified for which major uncertainties remain and for which additional experimental and theoretical work is recommended.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
259

22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

The information in this document has been funded by the United States Environmental Protection Agency under Interagency Agreement DW 930237 to the National Center for Atmospheric Research. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This study was carried out as part of the research effort of the National Center for Atmospheric Research in the development of a eulerian acid deposition model. It focuses upon the review and evaluation of the chemical reaction mechanisms and rate constants for the gas-phase reactions which generate the common tropospheric acids (sulfuric acid, nitric acid, hydrochloric acid, the organic acids (formic acid, acetic acid, etc.), and methane sulfonic acid). The evaluation expands on the mechanisms of Atkinson and Lloyd (1984), Leone and Seinfeld (1984), and others which were designed primarily for the use with photochemical smog models. A master mechanism is designed which treats the chemistry of the typical tropospheric reactants (nitrogen oxides, sulfur dioxide, ozone, hydrogen peroxide, ammonia, the simple amines, chlorine, hydrogen sulfide, dimethyl sulfide, the hydrocarbons (methane, ethane, propane, butane, 2,3-dimethylbutane, the C_5-C_8 alkanes, ethylene, propylene, trans-2-butene, isobutene, benzene, toluene, m-xylene, isoprene, alpha-pinene), and the variety of oxidation products of these species including the transient free radical species, aldehydes, ketones, hydroperoxides, and other species. Portions of the mechanism are identified for which major uncertainties remain and for which additional experimental and theoretical work is recommended.

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CHEMICAL TRANSFORMATION MODULES FOR EULERIAN ACID DEPOSITION MODEL

VOLUME I: THE GAS-PHASE CHEMISTRY

by

Professor J. Alistair Kerr[*]

Jack G. Calvert[**]

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[*] On leave from the Department of Chemistry, The University of Birmingham, Birmingham, England.

[**] Senior Scientist, Atmospheric Chemistry Division, The National Center for Atmospheric Research[***], Boulder, Colorado.

[***] The National Center for Atmospheric Research is sponsored by the U.S. National Science Foundation.

SECTION I

INTRODUCTION

As part of the research effort of the National Center for Atmospheric Research in the development of a Eulerian Acid Deposition Model, the present work was initiated to help formulate both gas-phase and liquid-phase chemical transformation mechanisms which are suitable for use in a chemical transformation module of the NCAR Acid Deposition Modeling Project. The several goals of the effort concerned with a chemical module development are outlined here:

THE GOALS:

To develop a gas- and aqueous-phase chemical transformation module that accurately treats:

1) gas-phase production of OH, HO_2, RO_2, H_2O_2, NO_3, N_2O_5, HNO_3, aldehydes, O_3, PAN, H_2SO_4, and other species that play a role in atmospheric acidification;

2) oxidation of dissolved SO_2 by: H_2O_2, O_3, O_2 and metal calalysts, and free radicals such as OH, HO_2, and RO_2;

3) aqueous phase production of H_2O_2;

4) effect of inhibitors (such as HCHO) and catalysts (such as metal ions) on the aqueous-phase oxidation of SO_2 by H_2O_2;

5) the role of PAN as an oxidizer of SO_2 and a contributor

to NO_3^- in rain;

6) aqueous-phase oxidation of nitrogenous compounds such as NO_2 and HONO;

7) mechanisms of gaseous and aqueous organic acid formation.

THE APPROACH:

1) Conduct a critical review of gas- and aqueous-phase chemistry which bears on the development of acids in the troposphere.

2) Develop a parameterized gas-phase chemical transformation module.

3) Check performance of the gas-phase mechanism against smog chamber data of surrogate HC/NO_x mixtures.

4) Develop a liquid-phase chemical reaction scheme and incorporate the scheme into the gas-phase module.

5) Conduct sensitivity studies on the combined gas- and aqueous-phase module to determine how uncertainties in input parameters impact on predictions of atmospheric acidification.

6) Make recommendations of kinetic and mechanistic data and/or atmospheric observations that are needed to reduce the uncertainties in the predictions.

The work which we describe in this volume of the report and in Volume II represents an important part of the total research effort of the NCAR chemical module development group. It relates primarily to the specific tasks outlined in items 1, 4 (first item), and 6 above. The other important aspects of the chemical module development, namely tasks 2, 3, 4 (second item) and 5 above, are proceeding concurrently largely through the efforts of William Stockwell and Christopher Walcek, with contributions from others of the Acid Deposition Modeling Group and the NCAR staff. Their efforts will be summarized in a separate, future report.

SECTION II

THE CHEMICAL MECHANISMS OF ACID GENERATION IN THE TROPOSPHERE

A. The Importance of Chemical Transformation Rates in the Development of Acid Deposition Models

Early signs of ecological damage have been observed in certain sensitive areas of the world which are deficient in soils with a good acid buffering capacity and which are recipients of a large input of acids through "acid rain" and/or dry deposition. Scientists throughout the world are actively working to assess the extent of damage which has occurred and that which can be expected in years ahead. Government leaders of many nations are attempting to evaluate alternative control strategies for acid deposition which can alleviate the existing and potential future problems.

The understanding of the nature and importance of the various chemical pathways to acid generation within the troposphere is one of the several prerequisites to the development of scientifically sound strategy for the control of acid deposition. Scientists now recognize that a large share of the acids deposited both in North America and in Europe originate from the oxidation of sulfur dioxide (SO_2) and the nitrogen oxides (nitric oxide (NO) and nitrogen dioxide (NO_2)) which are emitted from power plants, industrial operations, motor vehicles, and other fossil fuel combustion sources. These sources may be many hundreds of kilometers from the sites at which acid deposition eventually occurs.

The control of acid deposition is complicated by many factors which mirror our incomplete understanding of the subject. It is well established that the acids and the their precursor gases can be carried for great distances through the natural motions of the tropospheric air masses. Current models of long-range air transport do not allow an accurate description of the extent to which emissions from a specific source result in acid deposition at a given distant, sensitive receptor site. Of course such information is a very important input to the development of cost effective control strategies.

Most models which have been used in control strategy development do not attempt to incorporate the many complex chemical and physical processes which control acid generation, transport, and deposition. They often employ average wind flows, rather arbitrary, fixed or diurnaly varied rates of conversion of precursors to acids, and assumed rates of dry and wet deposition of acid precursors and acids. Such models are useful only for the control strategists in deriving very qualitative conclusions about the likely source regions which impact a sensitive area. However when such models are applied to estimate the acid deposition over large transport distances often involved in the acid deposition phenomenon in the eastern North America, the results can vary significanly from model to model (factors of 2-4 are not uncommon), and judgments based upon the results are of unpredictable quality.

Uncertainties in air mass motions over long times and great distances account for a large part of the variation seen in present model predictions. However uncertainties also arise as a consequence of the sensitivity of such models to the assumed chemical conversion rates. Thus Golomb et al. (1983) found that among the four basic steps of the transformation process in their analysis (acid generation rates, dry deposition of the precursors, dry deposition of the product acids, and wet deposition of the acids), the rate of acid generation is the most important factor in determining rain acidity. They concluded that accurate modeling must include time- and space-variability of the rates of acid generation.

The sensitivity of acid deposition to the rates of chemical generation of the acids results largely from the fact that the precursors of the acids and the acids themselves are not removed from the atmosphere with equal facility. Once sulfur dioxide is oxidized to sulfuric acid aerosol, it is dry deposited much less rapidly than is SO_2. If aerosols composed of sulfuric acid and its salts (ammonium bisulfate, ammonium sulfate, etc.) are incorporated into precipitating clouds, then the deposition of these species can be faster than that of gaseous SO_2. On the other hand, the nitric acid developed in the troposphere is much more rapidly deposited on the surface of the earth than is its precursors, NO and NO_2. Thus how much acid and the chemical nature of the acids deposited at sites many kilometers from the source of the precursors, are sensitive functions of the rates with which the acids are developed from the precursors.

B. General Features of the Chemical Mechanisms of Acid Generation

In recent years, the scientific community has made reasonable progress in elucidating the chemistry of the acid deposition problem, although many areas of uncertainty remain. For examples, see the studies of Atkinson et al. (1984); Brock and Durham (1984); Calvert and McQuigg (1975); Calvert et al. (1978); Calvert and Mohnen (1983); Calvert and Stockwell (1984); Calvert et al. (1984); Chameides and Davis (1982); Chang et al. (1981); Davis and Klauber (1975); Hoffmann and Jacob (1984); Leone and Seinfeld (1984); Logan et al. (1981); Martin (1984); NCAR (1983); Penkett et al. (1979); Sander and Seinfeld (1976); Schwartz (1984). There is general agreement that the major acids responsible for acid rain, sulfuric acid and nitric acid, are formed in the troposphere, largely through the oxidation of sulfur dioxide and oxides of nitrogen, respectively, through a variety of chemical reaction pathways. In recent years, the seemingly dominant role of the solution-phase reactions in acid rain development has been increasingly accepted. Indeed, the present authors share this view. However it is equally clear that the rates of acid generation in the troposphere through gas-phase chemistry can be significant, and many of the reactants that drive the SO_2 (HSO_3^-) oxidation in the solution phase of cloud water are generated through gas-phase chemistry. Obviously a scientifically sound description of both the gas-phase and aqueous-phase chemistry which develops acids in the troposphere is necessary in any model if computer simulations of acid development are to provide a realistic result which will be most useful in control strategy development.

The chemistry which is required to describe the many pathways to acid generation in the troposphere will be reviewed briefly in this section so that the inexperienced reader can appreciate the general aspects of the complex problem before exposure to the necessary detail of our indepth considerations in sections III and V (Volume II). There is general agreement that the major gas phase processes which lead to the formation of sulfuric acid and nitric acid in the troposphere arise from the reactions of the hydroxy (HO) radical with SO_2 and NO_2:

$SO_2 + HO\ (+ M) \dashrightarrow HOSO_2\ (+ M)$

$HOSO_2 + O_2 \dashrightarrow HO_2 + SO_3\ (\dashrightarrow H_2SO_4)$

$NO_2 + HO\ (+ M) \dashrightarrow HONO_2\ (+ M)$

Thus it is very important to formulate a reaction scheme which describes well the generation and destruction modes of the HO-radical. Through the years a variety of excellent studies have focussed on the chemistry of the hydrocarbon-nitrogen oxide-polluted atmosphere; much of the important chemistry of these mixtures is related directly to the HO-radical chemistry. Such studies have shown that a major, but not exclusive, source of the HO-radical is the photolysis of the ozone molecule:

$O_3 + h\nu \rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow 2HO$

$O(^1D) + M\ (N_2,\ O_2) \rightarrow O(^3P) + M\ (N_2, O_2)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$

The concentration of ozone in the troposphere is not only important as a reactant to form HO-radicals, but ozone itself is a good reactant to oxidize dissolved SO_2 in cloud, fog, and rain water. Thus care must be exercised in the design of chemical mechanisms to simulate acid generation in the troposphere to insure that ozone generation is estimated with reasonable accuracy. A great deal of work has been carried out in the development of such models, and advantage of these studies can be taken in our model development. For examples, see Atkinson et al., 1982; Atkinson and Lloyd, 1984; Killus and Whitten, 1983; Graedel and Schiavone, 1981; Leone and Seinfeld, 1984; McRae et al., 1982.

The basic chemistry which occurs on irradiation of hydrocarbon-NO_x mixtures in the troposphere determines the ozone level which develops. The hydrocarbons (RH), aldehydes (RCHO), carbon monoxide (CO), and other partially oxidized organic species act as reactants toward HO radicals; HO_2 and RO_2 radicals are formed, and these react in chain reactions to reform HO radicals and oxidize NO to NO_2 in a repeating series of reactions:

$HO + RH \rightarrow H_2O + R$

$R + O_2 \rightarrow RO_2$

$RO_2 + NO \rightarrow RO + NO_2$

$RO + O_2 \rightarrow HO_2 + R'CHO$

$HO_2 + NO \rightarrow HO + NO_2$

These reactions are very important in establishing the levels of ozone generated, since a major source of ozone in the troposphere is the photolysis of NO_2, and its major sink in the polluted troposphere is its reaction with NO:

$NO_2 + hv \rightarrow NO + O(^3P)$

$O(^3P) + O_2 + M \rightarrow O_3 + M$

$NO + O_3 \rightarrow NO_2 + O_2$

During the daylight hours, the above sequence of reactions establishes an ozone concentration which is roughly proportional to the intensity of the sunlight which drives the NO_2 photodissociation and the $[NO_2]/[NO]$ ratio. Thus as the hydrocarbon-HO-HO_2-RO_2reaction sequence effects the conversion of NO to NO_2, the ozone level rises to reflect the occurrence of the NO-NO_2-O_3 reactions. The reaction of each hydrocarbon (RH) with the HO radical has a different rate constant. Each RO_2 radical formed subsequently oxidizes NO to NO_2 and generates an alkoxy radical

(RO), or, in a competitive reaction, it forms organic nitrates. These reactions have relative efficiencies which vary markedly with the structure of the hydrocarbon radical (R). The different alkoxy radicals react with oxygen, decompose or rearrange to generate HO_2 radicals, new alkylperoxy radicals, aldehydes, ketones, etc., each of which have a unique facility to oxidize additional NO molecules or generate new peroxy radicals through other thermal and photochemical processes. Hence each hydrocarbon molecule has a different facility with which it contributes to the generation of ozone. Thus it is very important to characterize the hydrocarbon reactivities well in any model if one hopes to predict well the concentrations of ozone, HO radicals, HO_2 radicals, and other reactants and products of the reactions of the polluted troposphere. This is a non-trivial task, since there are literally thousands of different hydrocarbons present in a polluted air mass, and some means of mechanism simplification is necessary to have a workable model of reasonable complexity.

The solution-phase reactions which lead to the oxidation of dissolved sulfur dioxide (HSO_3^-) involve several important oxidants in addition to ozone. Thus evidence suggests strongly that hydrogen peroxide, organic peroxides, peroxyacylnitrates as well as HO_2 and HO-radicals can be very important for acid generation when cloud, fog, or rain water is available to absorb these reactants and SO_2 in sufficient quantity. All of these reactants are generated in gas phase reactions which are controlled by the same complex hydrocarbon-NO_x chemistry which we described briefly in regard to ozone generation.

The hydrogen peroxide molecule (H_2O_2) is the most important of the liquid-phase oxidants for SO_2 in aqueous solutions (HSO_3^-) for many of the atmospheric conditions encountered in the troposphere. It is generated through the self-reactions of the HO_2 radical:

$HO_2 + HO_2$ (+M) --> $H_2O_2 + O_2$ (+M)

$HO_2 + H_2O$ <=> $HO_2.H_2O$

$HO_2 + HO_2.H_2O$ (+M) --> $H_2O_2 + O_2 + H_2O$ (+M)

The organic hydroperoxides which also oxidize HSO_3^- effectively, form in a similar series of related reactions involving the peroxyacyl radicals (RO_2) and the HO_2 radicals:

$RO_2 + HO_2$ --> $RO_2H + O_2$

Thus it is extremely important that the gas-phase processes which create the HO_2 and RO_2 radicals do so at rates which are realistic.

Acetaldehyde (CH_3CHO) and the higher aldehydes (RCHO) react with HO radicals to form ultimately the peroxyacylnitrates ($RCOO_2NO_2$) of which peroxyacetylnitrate ($CH_3COO_2NO_2$) is the simplest member of the series.

$CH_3CHO + HO$ --> $H_2O + CH_3CO$

$CH_3CO + O_2$ --> CH_3COO_2

$CH_3COO_2 + NO_2$ --> $CH_3COO_2NO_2$

These compounds also oxidize bisulfite ion (HSO_3^-) effectively when dissolved in the aqueous-phase.

The free radicals such as HO and HO_2 generated in the gas-phase reactions, can be captured by cloud droplets, and they may act also as effective oxidizing agents to form sufuric acid from the bisulfite ion in solution. In the case of the HO_2 radicals, their transfer to the solution phase introduces new reaction pathways to form H_2O_2 (Chameides and Davis, 1982; Schwartz, 1984):

$$2\ HO_2(aq) \longrightarrow H_2O_2(aq)$$

$$HO_2(aq) + O_2^-(aq) \longrightarrow HO_2^-(aq) + O_2(aq)$$

$$HO_2^-(aq) + H_2O(aq) \Longleftrightarrow H_2O_2(aq) + OH^-(aq)$$

Additional gas phase reactions generate the NO_3 radical and the N_2O_5 molecule which, through transfer to cloud water, create additional nitric acid:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$

$$NO_2 + NO_3\ (+\ M) \longrightarrow N_2O_5\ (+\ M)$$

$$N_2O_5 + H_2O(\text{cloud}) \longrightarrow 2HONO_2(\text{in cloud water})$$

Formic acid, acetic acid, and the higher molecular weight organic acids, are the products of both gas-phase and liquid-phase reactions. A proper evaluation of these species in acid deposition modeling requires that the model predict well the several precursors to these acids (ozone, alkenes, aldehydes, etc.).

In natural emissions there are sulfur compounds other than SO_2, e.g., hydrogen sulfide (H_2S), dimethyl sulfide (CH_3SCH_3), etc., which also oxidize to form acidic species (CH_3SO_3H, H_2SO_4, etc.). Also there are natural and anthropogenic emissions of acid-neutralizing species such as ammonia (NH_3) and organic amines (e.g., CH_3NH_2). These species must be included in the chemical mechanism of acid deposition models if proper account is to be taken of the natural input to acid rain.

From this very brief description it should be evident that the oxidation of sulfur dioxide to sulfuric acid, nitrogen oxides to nitric acid, and organic compounds to organic acids in the troposphere involves a very complex series of coupled gas-phase and liquid-phase reactions among hydrocarbons, the hydrocarbon oxidation products (aldehydes, organic peroxides, etc.), the sulfur and nitrogen oxides, and other reactive species as well as the intensity of the sunlight. The task of developing a realistic yet simplified reaction scheme which can account for the major reactants of acid generation well is a nontrivial task.

It is the primary goal of this work to review in depth and to evaluate the present state of our knowledge of the detailed chemistry which controls acid development in the troposphere and to identify remaining areas of research which are required to solve the seemingly important remaining problems related to the reaction mechanism. In section III we review and evaluate the homogeneous gas phase chemistry which we identify as potentially significant for the development of acids in the troposphere. In section IV we summarize what we feel are the most important areas of uncertainty for which additional experimental and theoretical work should be encouraged. In Appendix A of this volume the master mechanism of the gas-phase chemistry is given. Here the methods outlined in the section III have been applied to derive estimates of the rate contants for the relatively large number of reactants included in the master mechanism.

SECTION III

REVIEW AND EVALUATION OF THE MECHANISM AND RATE CONSTANTS FOR THE HOMOGENEOUS GAS-PHASE CHEMISTRY OF THE TROPOSPHERIC ACID GENERATION

A) Introduction

In section II we have described how the chemistry which controls acid generation in the troposphere is related closely to the chemistry of "smog" generation within the polluted troposphere. For over thirty years many scientists have studied the detailed chemistry of the polluted troposphere, and many different approaches to the modeling of these chemical changes have developed. The most recent useful chemical mechanisms for modeling the troposphere chemical changes employ either rather detailed, explicit chemistry (e.g., see the study of Atkinson and Lloyd, 1984) or "lumped" chemical processes which attempt to simplify the complex chemistry in a fewer number of seemingly realistic yet generalized chemical reactions (e.g., see Killus and Whitten, 1982, 1983). Of course the final chemistry module to be used in our Eulerian Acid Deposition Model must be highly simplified in order to conserve computer time and allow efficient operation of the model. However in any simplification which we make in pruning the more complete mechanism, we do not wish to sacrifice the scientific integrity of the model and its ability to predict the rates of acid generation with reasonable accuracy. We have concluded that the only way we can judge properly the performance of the simplified mechanism and test adequately the scientific accuracy of any highly abbreviated chemistry reaction scheme for acid development, is to start from a rather complete and scientifically sound reaction scheme which defines well the detailed, relevant chemical processes which occur in the troposphere. Of course this scheme should be adequately tested or verified through simulations of actual rate data derived from both simple and complex reaction mixtures under conditions which simulate those of the troposphere.

B) The Explicit Mechanism of Leone and Seinfeld

The evaluation of rate and reaction mechanisms conducted by Atkinson and Lloyd (1984) appears to us to be the most thoroughly documented and scientifically accurate evaluation from which we could start our chemical mechanism development. Recently Leone and Seinfeld (1984) have utilized this evaluation to develop a somewhat simplified "Explicit Mechanism" which they then employed to carry out a comparative analysis of various simplified reaction schemes now used in modeling smog chemistry. As a reasonable starting point for our model development, we have evaluated the various component reactions in the Leone and Seinfeld adaptation of the Atkinson and Lloyd evaluation. We have summarized these considerations in Table I where for each of the reactions a comparison is shown between rate constant estimates accepted by Leone and Seinfeld [1], Lurmann, Lloyd, and Atkinson [2], Atkinson and Lloyd [3], Whitten, Killus and Johnson [4], the NASA Panel for Data Evaluation [5] and the CODATA Task Group on Chemical Kinetics [6]. Our recommended rate constant choice based upon our evalution is also shown in the Table I. The comments and notes which are referenced in the table follow the table itself. These explain briefly the reasoning used in deriving our rate constant choice. This comparison allows a rather quick review of the current relevent rate data which we will describe in greater detail later in this section. Several inorganic reactions involving NO_x and SO_2 chemistry, not included in the Leone and Seinfeld "Explicit Mechanism", are added at the end of the reaction sequence summarized in Table I. It will be apparent to the reader who studies the summary of reaction rate data given in Table I, that in general these data, suggested by the various authoritative sources, are in reasonable accord. In many cases our rate constant choice is the same or very similar to that suggested by Atkinson and Lloyd and Leone and Seinfeld. However there are some significant differences which can be noted in Table I.

Table I. Comparison of Rate Constants for the Reactions in the Leone and Seinfeld "Explicit Mechanism" [1]

Reaction	L&S(1)		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)*							(E/R)/K			
Inorganic Reactions:												
1) $NO_2+h\nu\rightarrow NO+O(^3P)$	---	---	---	---	---	---	---	---	---	---	-	
2) $O(^3P)+O_2\rightarrow O_3$	$-5.1x10^{2}$	$1.8x10^{-14}$	---	$1.5x10^{-14}$	$1.5x10^{-14}$	$1.5x10^{-14}$	$1.3x10^{-14}$	$1.5x10^{-14}$	$-5.6x10^{2}$	NASA[5]	-	
3) $O_3+NO\rightarrow NO_2+O_2$	$1.5x10^{3}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.8x10^{-14}$	$1.37x10^{3}$	NASA[5]	-	
4) $O(^3P)+NO_2\rightarrow NO+O_2$	---	$9.5x10^{-12}$	---	$9.3x10^{-12}$	$9.3x10^{-12}$	$9.3x10^{-12}$	$9.3x10^{-12}$	$9.3x10^{-12}$	---	NASA[5]	-	
5) $O_3+NO_2\rightarrow NO_3+O_2$	$2.45x10^{3}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$3.2x10^{-17}$	$2.45x10^{3}$	NASA[5]	-	
6) $NO_3+NO\rightarrow 2NO_2$	---	$2.0x10^{-11}$	$1.9x10^{-11}$	$1.9x10^{-11}$	$2.0x10^{-11}$	$2.0x10^{-11}$	$2\ \ x10^{-11}$	$2.0x10^{-11}$	---	NASA[5]	-	
7) $HO_2+NO_2\rightarrow HO_2NO_2$	---	$1.1x10^{-12}$	$1.2x10^{-12}$	$1.4x10^{-12}$	$1.5x10^{-12}$	$1.5x10^{-12}$	$9.9x10^{-13}$	$9.9x10^{-13}$	$-6.9x10^{2}$	CODATA[6]	1	
8) $NO_2+OH\rightarrow HNO_3$	---	$1.1x10^{-11}$	$1.2x10^{-11}$	$1.1x10^{-11}$	$1.2x10^{-11}$	$1.1x10^{-11}$	$1.6x10^{-11}$	$1.1x10^{-11}$	---	NASA[5]	-	
9) $O_3+OH\rightarrow HO_2+O_2$	$9.7x10^{2}$	$6.7x10^{-14}$	$6.8x10^{-14}$	$6.8x10^{-14}$	$6.8x10^{-14}$	$6.8x10^{-14}$	$6.7x10^{-14}$	$6.8x10^{-14}$	$9.4x10^{2}$	NASA[5]	-	
10) $O_3+HO_2\rightarrow OH+2O_2$	$5.8x10^{2}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$2.0x10^{-15}$	$5.8x10^{2}$	NASA[5]	-	
11) $HO_2NO_2\rightarrow HO_2+NO_2$	$1.042x10^{4}$	$8.5x10^{-2}$	$7.2x10^{-2}$	$8.5x10^{-2}$	$9.1x10^{-2}$	---	$5.3x10^{-2}$	$5.3x10^{-2}$	$9.9x10^{3}$	CODATA[6]	-	
12) $HO_2+NO\rightarrow NO_2+OH$	$-2.4x10^{2}$	$8.1x10^{-12}$	$8.3x10^{-12}$	$8.3x10^{-12}$	$8.3x10^{-12}$	$8.3x10^{-12}$	$8.3x10^{-12}$	$8.3x10^{-12}$	$-2.4x10^{2}$	NASA[5]	-	
13) $HO_2+HO_2\rightarrow H_2O_2+O_2$	$-1.2x10^{3}$	$2.6x10^{-12}$	$2.8x10^{-12}$	$2.8x10^{-12}$	$2.8x10^{-12}$	$2.8x10^{-12}$	$2.8x10^{-12}$	$2.8x10^{-12}$	See note	NASA[5]	2	
14) $HO_2+HO_2+H_2O\rightarrow H_2O_2+O_2+H_2O$	$-5.8x10^{3}$	$6.1x10^{-30}$	$4.7x10^{-12}$	$6\ \ x10^{-30}$	$5.0x10^{-30}$	---	complex fn	See note	See note	---	2	Sander et al.[7]
15) $O_3+h\nu\rightarrow O(^3P)+O_2$	---	$1.1x10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
16) $O_3+h\nu\rightarrow O(^1D)+O_2$	---	$4.7X10^{-5}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
17) $O(^1D)+O_2/N_2(air)\rightarrow O(^3P)+O_2/N_2$	---	$2.9x10^{-11}$	---	$2.9x10^{-11}$ (air)	$2.9x10^{-11}$	$2.9x10^{-11}$	$2.9x10^{-11}$	$2.9x10^{-11}$	---	NASA[5]	2a	

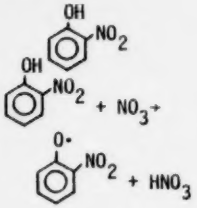
*Units apply to second order reactions; the few third order and first order reactions use $cm^6\ molec^{-2}\ s^{-1}$ and s^{-1}, respectively.

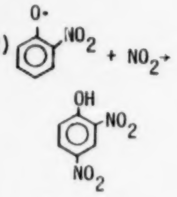
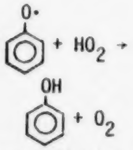
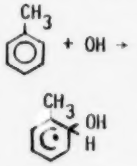
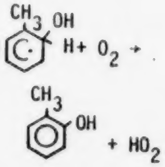
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule^{-1} s^{-1} (298K 1 atm air)							(E/R)/K			
18) $O(^1D)+H_2O \rightarrow 2OH$	---	$2.2x10^{-10}$	---	$2.2x10^{-10}$	$2.2x10^{-10}$	$2.2x10^{-10}$	$2.2x10^{-10}$	$2.2x10^{-10}$	---	NASA[5]	-	
19) $NO+OH \rightarrow HONO$	---	$6.6x10^{-12}$	$6.7x10^{-12}$	$6.6x10^{-12}$	$4.7x10^{-12}$	$4.8x10^{-12}$	$4.2x10^{-12}$	$4.8x10^{-12}$	---	NASA[5]	-	
20) $HONO+h\nu \rightarrow NO+OH$	---	$3.0x10^{-3} k_{NO_2}$	---	---	---	---	---	---	---	---	-	
21) $NO+NO+O_2 \rightarrow 2NO_2$	$-5.3x10^2$	$2.0x10^{-38}$ $[O_2]$	---	$2.0x10^{-38}$ $[O_2]$	$2.0x10^{-38}$ $[O_2]$	---	---	$2.0x10^{-38}$ $[O_2]$	$-5.3x10^2$	---	-	Hampson&Garvin [8]
22) $NO_3+NO_2 \rightarrow NO+NO_2+O_2$	$1.23x10^3$	$4.0x10^{-16}$	$4.0x10^{-16}$	$4.0x10^{-16}$	---	---	---	$4.0X10^{-16}$	$1.23X10^3$	A&L[3]	-	
23) $NO_3+NO_2 \rightarrow N_2O_5$	---	$1.1X10^{-12}$	$1.3X10^{-12}$	$1.2X10^{-1}$	$8.6X10^{-1}$	$8.6X10^{-13}$	$1.2X10^{-12}$	$1.2X10^{-12}$	$6.0X10^1$	---	3	Perner et al. [9]
24) $N_2O_5 \rightarrow NO_2+NO_3$	---	$5.2X10^{-2}$	$6.9X10^{-2}$	$4.6X10^{-2}$	$4.5X10^{-2}$	---	$5.2X10^{-2}$	$5.2X10^{-2}$	$1.084X10^4$	---	3	Perner et al. [9]
$K_{eq}, N_2O_5 \rightleftharpoons NO_2+NO_3$	---	$4.73X10^{10}$	$5.3X10^{10}$	$5.2X10^{10}$	$5.2X10^{10}$	---	$4.3X10^{10}$	---	---	---	-	
25) $N_2O_5+H_2O \rightarrow 2\ HNO_3$	---	0.0	$1.3X10^{-21}$	$1.3X10^{-21}$	$1.0X10^{-20}$	---	---	0	---	A&L[3]	-	
26) $H_2O_2+OH \rightarrow HO_2+H_2O$	---	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.7X10^{-12}$	$1.87X10^2$	NASA[5]	-	
27) $H_2O_2+h\nu \rightarrow 2\ OH$	---	$8.4X10^{-4} k_{NO_2}$	---	---	---	---	---	---	---	---	-	
28) $CO+OH \xrightarrow{O_2} HO_2+CO_2$	---	$2.7X10^{-13}$	$2.2X10^{-13}$	$2.2X10^{-13}$	$2.7X10^{-13}$	$2.4X10^{-13}$	$2.2X10^{-13}$	$2.4X10^{-13}$	---	NASA[5]	-	
29) $NO_3+h\nu \rightarrow 0.3NO + 0.7NO_2+0.7O(^3P)$	---	$1.55X10^1 k_{NO_2}$	---	---	---	---	---	---	---	---	-	
Aldehyde Reactions and PAN Formation:												
30) $CH_3CHO+h\nu \xrightarrow{2O_2} CH_3O_2\cdot+HO_2+CO$	---	$2.58X10^{-4} k_{NO_2}$	---	---	---	---	---	---	---	---	-	

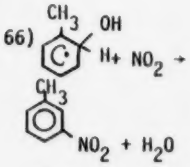
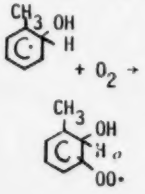
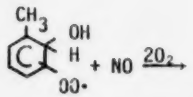
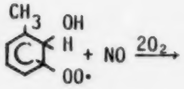
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
31) $CH_3CHO + OH \xrightarrow{O_2} CH_3C(O)O_2\cdot + H_2O$	-2.6×10^{2}	1.6×10^{-11}	1.6×10^{-11}	1.6×10^{-11}	1.6×10^{-11}	---	1.6×10^{-11}	1.6×10^{-11}	-2.6×10^{2}	CODATA[6]	-	
32) $CH_3O_2\cdot + NO \rightarrow NO_2 + CH_3O\cdot$	---	7.4×10^{-12}	7.6×10^{-12}	7.6×10^{-12}	7.4×10^{-6}	7.6×10^{-12}	7.6×10^{-12}	7.6×10^{-12}	-1.8×10^{2}	NASA[5]	-	
33) $CH_3O\cdot + O_2 \rightarrow HCHO + HO_2$	1.35×10^{3}	1.4×10^{-15}	---	1.3×10^{-15}	1.3×10^{-15}	1.3×10^{-15}	1.3×10^{-15}	1.3×10^{-15}	1.31×10^{3}	NASA[5]	-	
34) $CH_3O\cdot + NO_2 \rightarrow CH_3ONO_2$	---	1.5×10^{-11}	---	1.5×10^{-11}	1.5×10^{-11}	---	1.2×10^{-11}	1.5×10^{-11}	---	A&L[3]	11	
35) $CH_3O_2\cdot + HO_2 \rightarrow CH_3OOH + O_2$	-1.3×10^{3}	6.2×10^{-12}	---	---	6.0×10^{-12}	6.0×10^{-12}	6.5×10^{-12}	1.5×10^{-12}	---	---	12	
36) $CH_3C(O)O_2\cdot + NO \xrightarrow{2O_2} NO_2 + CH_3O_2\cdot + CO_2$	---	7.4×10^{-12}	7.6×10^{-12}	7.6×10^{-12}	1.1×10^{-11}	---	1.4×10^{-11}	1.0×10^{-11}	---	---	13	
37) $CH_3C(O)O_2\cdot + NO_2 \rightarrow PAN$	---	4.7×10^{-12}	4.7×10^{-12}	4.7×10^{-12}	6.1×10^{-12}	---	6×10^{-12}	6.0×10^{-12}	---	CODATA[6]	-	
38) $CH_3C(O)O_2\cdot + HO_2 \rightarrow CH_3C(O)O_2H + O_2$	---	3.0×10^{-12}	---	---	6.5×10^{-12}	---	---	1.5×10^{-12}	---	---	12	
39) $PAN \rightarrow CH_3C(O)O_2\cdot + NO_2$	1.354×10^{4}	3.7×10^{-4}	3.6×10^{-4}	3.6×10^{-4}	3.7×10^{-4}	---	4.2×10^{-4}	4.2×10^{-4}	1.333×10^{4}	CODATA[6]	-	

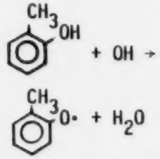
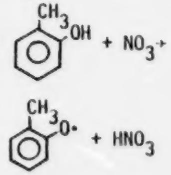
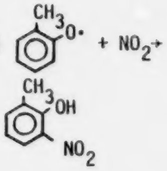
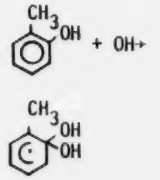
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
40) $HCHO+h\nu \rightarrow H_2+CO$	---	$3.3X10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
41) $HCHO+h\nu \xrightarrow{2O_2} 2\ HO_2 + CO$	---	$2.35X10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
42) $HCHO+OH \xrightarrow{O_2} HO_2+CO+H_2O$	---	$1.1X10^{-11}$	$1.0X10^{-11}$	$1.0X10^{-11}$	$1.0X10^{-11}$	$1.0X10^{-11}$	$1.1X10^{-11}$	$1.0X10^{-11}$	---	NASA[5]	-	
42a) $HCHO+NO_3 \rightarrow HCO+HONO_2$	---	---	$3.2X10^{-16}$	$3.2X10^{-16}$	$2.1X10^{-18}$	---	---	$6.3X10^{-16}$	---	---	14	Cantrell *et al.*[10]
α-Dicarbonyl Chemistry:												
43) $CH_3C(O)CHO + OH \xrightarrow{O_2} CH_3C(O)O_2\cdot + CO + H_2O$	---	$1.7X10^{-11}$	---	$1.7X10^{-11}$	---	---	---	$1.7X10^{-11}$	---	Exptl value(A&L)	-	
44) $CH_3C(O)CHO + h\nu \xrightarrow{2O_2} CH_3C(O)O_2\cdot + HO_2 + CO$	---	$1.3X10^{-2}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
45) $CH_3C(O)CHO + h\nu \xrightarrow{2O_2} CH_3O_2\cdot + HO_2 + 2CO$	---	$6.0X10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
46) $(CHO)_2 + OH \xrightarrow{O_2} HO_2+2CO+H_2O$	---	$1.2X10^{-11}$	---	$1.2X10^{-11}$	---	---	---	$1.2X10^{-11}$	---	Exptl value(A&L)		

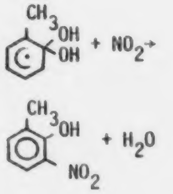
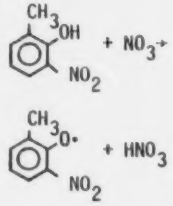
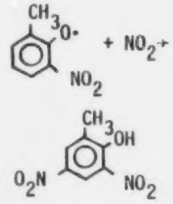
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
47) $(CHO)_2 + h\nu \rightarrow 0.13HCHO + 0.87H_2 + 1.87CO$	---	$8.0X10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
Toluene Abstraction Pathway:												
48) $C_6H_5\text{-}CH_3 + OH \xrightarrow{O_2} C_6H_5\text{-}CH_2O_2\cdot + H_2O$	---	$5.1X10^{-13}$	$4.9X10^{-13}$	$5.1X10^{-13}$	$5.1X10^{-13}$	---	---	$5.1X10^{-13}$	---	Exptl value(A&L)	-	
49) $C_6H_5\text{-}CH_2O_2\cdot + NO \rightarrow NO_2 + C_6H_5\text{-}CH_2O\cdot$	---	$6.1X10^{-12}$	$6.9X10^{-12}$	$6.3X10^{-12}$	---	---	---	$6.3X10^{-12}$	$-1.8X10^{2}$	Based on $RO_2+NO \rightarrow RO+NO_2$(A&L)	-	
50) $C_6H_5\text{-}CH_2O_2\cdot + NO \rightarrow C_6H_5\text{-}CH_2ONO_2$	---	$6.8X10^{-13}$	$7.6X10^{-13}$	$7.0X10^{-13}$	---	---	---	$7.0X10^{-13}$	---	Based on approx.exptl ratio(A&L)	-	
51) $C_6H_5\text{-}CH_2O\cdot + O_2 \rightarrow C_6H_5\text{-}CHO + HO_2$	$6.9X10^{2}$	$6.8X10^{-15}$	---	$7\ X10^{-15}$	---	---	---	$1.1X10^{-14}$	$5.5X10^{2}$	$\Delta H=-34.2$ kcal mol^{-1}	15	
52) $C_6H_5\text{-}CH_2O\cdot + NO_2 \rightarrow C_6H_5\text{-}CH_2ONO_2$	---	$1.3X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	---	-	
53) $C_6H_5\text{-}CHO + h\nu \rightarrow$ stable products	---	$1.6X10^{-3}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
54) $C_6H_5\text{-}CHO + OH \xrightarrow{O_2} C_6H_5\text{-}C(O)O_2\cdot + H_2O$	---	$1.3X10^{-11}$	---	$1.2X10^{-11}$	$1.4X10^{-11}$	---	---	$1.2X10^{-11}$	---	cf.with OH+RCHO (A&L)		

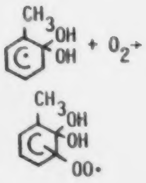
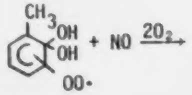
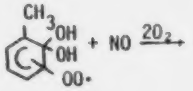
Reaction	L&S[1] (E/R)/K	L&S[1]	LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work	This Work (E/R)/K	Comments	Notes	References
		k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)										
55) C_6H_5-C(0)O_2•+ NO $\xrightarrow{O_2}$ NO_2+C_6H_5-O_2• +CO_2	---	$6.8X10^{-12}$	---	7 $X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^{2}$	Based on RO_2+NO→ RO+NO_2(A&L)	-	
56) C_6H_5-C(0)O_2•+ NO_2→C_6H_5-C(0)O_2NO_2	---	$4.7X10^{-12}$	---	$4.7X10^{-12}$	$1.7X10^{-12}$	---	---	$6.0X10^{-12}$	---	cf.CH_3COO_2+ NO_2		
57) C_6H_5-C(0)O_2NO_2→ C_6H_5-C(0)O_2•+NO_2	$1.304X10^{4}$	$1.6X10^{-4}s^{-1}$	---	$1.6X10^{-4}s^{-1}$	---	---	---	$1.8X10^{-4}s^{-1}$	$1.28X10^{4}$	---	16	Ohta and Mizoguchi [24] Kenley and Hendry [25]
58) C_6H_5-O_2•+NO→ NO_2+C_6H_5-O•	---	$6.1X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^{2}$	cf.RO_2+ NO→RO+NO_2		
59) C_6H_5-O_2•+NO_2→ NO_3+C_6H_5-O•	---	$6.8X10^{-12}$	---	$4.7X10^{-12}$	---	---	---	$6.0X10^{-12}$	---	via PAN decomposition	17	
60) C_6H_5-O•+NO_2→	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	cf.RO+NO_2 (A&L)		
61) 	---	$2.0X10^{-12}$	---	---	---	---	---	$3.7X10^{-12}$	---	---	14	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
62) 	---	1.5X10^{-11}	---	1.5X10^{-11}	---	---	---	1.5X10^{-11}	---	cf.RO+NO$_2$ (A&L)	-	
63) 	---	5.0X10^{-12}	---	5 X10^{-12}	---	---	---	5.0X10^{-12}	---	cf.CH$_3$O+ HO$_2$ (A&L)	-	
Toluene Addition Pathway:												
64) 	---	5.9X10^{-12}	---	5.9X10^{-12}	---	---	---	5.9X10^{-12}	-8.1X10^{2}	Exptl value (A&L)	-	
65) 	6.9X10^{2}	6.8X10^{-15}	---	7 X10^{-15}	---	---	---	7 X10^{-15}	5 X10^{2}	cf.RO+O$_2$→ $>C=O+HO_2$ (A&L)	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
66) 	---	$3.0X10^{-11}$	---	$3.1X10^{-11}$	---	---	---	$3.1X10^{-11}$	---	Exptl k_{65}/k_{66}= $4.4X10^3$ (A&L)	-	
67) 	---	$3.3X10^{-14}$	---	$3.3X10^{-15}$	---	---	---	$3.3X10^{-15}$	---	Exptl product ratio (A&L) discrepancy between L&S[1] and A&L [3]		
68)  $NO_2+HO_2+CH_3C(O)CHO+$ $CH(O)CH=CHCHO$		$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$RO_2+NO\rightarrow$ $RO+NO_2$	26	
69)  $NO_2+HO_2+(CHO)_2$ $+CH_3C(O)CH=CHCHO$		0	---	---	---	---	---	---	---	---	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	$k/cm^3\ molecule^{-1}\ s^{-1}$ (298K 1 atm air)							(E/R)/K			
Toluene Addition Path (continued)												
70)  CH_3 OH + OH → CH_3 O· + H_2O	$9.0X10^2$	$3.3X10^{-12}$	---	$3.3X10^{-12}$	---	---	---	$3.3X10^{-12}$	$9.0X10^2$	Exptl (A&L)	-	
71)  CH_3 OH + NO_3→ CH_3 O· + HNO_3	---	$1.0X10^{-11}$	---	$1.2\ 10^{-11}$	---	---	---	$2.2X10^{-11}$	---	---	14	
72)  CH_3 O· + NO_2→ CH_3 OH NO_2	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	cf.RO+NO_2→ $RONO_2$(A&L)		
73)  CH_3 OH + OH→ CH_3 OH OH	---	$3.8X10^{-11}$	---	$3.8X10^{-11}$	---	---	---	$3.8X10^{-11}$	---	Exptl (A&L)		

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
74) 	---	$3.0X10^{-11}$	---	$3.1X10^{-11}$	---	---	---	$3.1X10^{-11}$	---	See reaction (66)(A&L)	-	
75) 	---	$1.0X10^{-11}$	---	$1.0X10^{-11}$	---	---	---	$1.8X10^{-11}$	---	---	14	
76) 	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	See reaction (72)(A&L)	-	

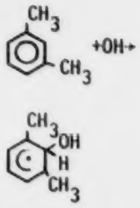
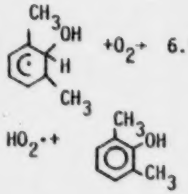
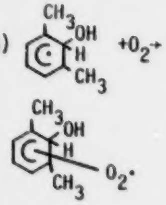
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
77) 	---	$3.3X10^{-14}$	---	$3.3X10^{-15}$	---	---	---	$3.3X10^{-15}$	---	See reaction (67)(A&L) Discrepancy between L&S[1] and A&L[3]	-	
78)  $NO_2 + HO_2$ $+ CH(O)CH{=}CHCHO$ $+CH_3C(O)COOH$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$RO_2+NO \rightarrow RO+NO_2$	26	
79)  $NO_2 + HO_2$ $+CH_3C(O)CH{=}CHCHO$ $+CH(O)COOH$	---	0	---	---	---	---	---	---	---	---	26	

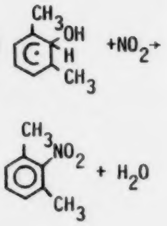
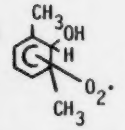
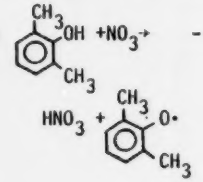
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
80) $CH(O)COOH+OH \xrightarrow{O_2} HO_2+H_2O+CO+CO_2$	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	est. cf. OH+RCHO (A&L)	-	
81) $CH_3C(O)COOH+h\nu \rightarrow CH_3CHO+CO_2$	---	$1.4X10^{-2}k_{NO_2}$	---	---	---	---	---	---	---	---	-	
Conjugated γ-dicarbonyl chemistry												
82) $HC(O)CH=CHCHO+OH \xrightarrow{O_2} HC(O)CH=CHC(O)O_2\cdot+H_2O$	---	$3.0X10^{-11}$	---	$3.0X10^{-11}$	---	---	---	$3.0X10^{-11}$	---	est. cf. OH+RCHO (A&L)	-	
83) $HC(O)CH=CHC(O)O_2\cdot+NO \xrightarrow{O_2} NO_2+CO_2+HC(O)CH=CHO_2\cdot$		$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	$C_4O_2+NO \rightarrow RO+NO_2$	18	
84) $HC(O)CH=CHO_2\cdot+NO \xrightarrow{O_2} NO_2+HC(O)CH(O_2\cdot)CHO$	---	$6.8X10^{-12}$	---	$6.7X10^{-12}$	---	---	---	$7.3X10^{-12}$	$-1.8X10^2$	$C_3O_2+NO \rightarrow RO+NO_2$	18	
85) $HC(O)CH(O_2\cdot)CHO+NO \rightarrow HC(O)CH(ONO_2)CHO$	---	$2.7X10^{-13}$	---	$3X10^{-13}$	---	---	---	$2.9X10^{-13}$	---	$C_3O_2+NO \rightarrow C_3ONO_2$	18	
86) $HC(O)CH=CHC(O)O_2\cdot+NO_2 \rightarrow HC(O)CH=CHCO_3NO_2$		$4.7X10^{-12}$	---	$4.7X10^{-12}$	---	---	---	$6.0X10^{-12}$	---	cf. $CH_3COO_2+NO_2 \rightarrow PAN$ (CODATA[6])		

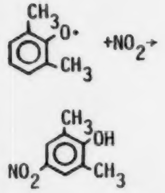
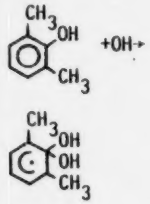
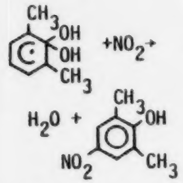
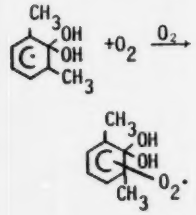
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
87) $HC(O)CH{=}CHCO_3NO_2 \rightarrow HC(O)CH{=}CHC(O)O_2{\cdot}+NO_2$		$3.7\times10^{-4}\ s^{-1}$	---	3.6×10^{-4}	---	---	---	4.2×10^{-4}	1.333×10^{4}	cf. $PAN \rightarrow CH_3COO_2 + NO_2$ (CODATA[6])	-	
88) $HC(O)CH(O_2{\cdot})CHO + NO \xrightarrow{O_2} (CHO)_2 + HO_2 + NO_2 + CO$		6.8×10^{-12}	---	6.7×10^{-12}	---	---	---	7.3×10^{-12}	-1.8×10^{2}	$C_3O_2 + NO \rightarrow RO + NO_2$	18	
89) $HC(O)CH{=}CHO_2{\cdot} + NO \rightarrow HC(O)CH{=}CHONO_2$	---	2.7×10^{-13}	---	3×10^{-13}	---	---	---	2.9×10^{-13}	---	$C_3O_2 + NO \rightarrow C_3ONO_2$	18	
90) $HC(O)CH{=}CHO_2{\cdot} + NO_2 \xrightarrow{O_2} HC(O)CH(O_2{\cdot})CHO + NO_3$	---	6.8×10^{-12}	---	$7\ \times10^{-12}$	---	---	---	6.8×10^{-12}	---	via PAN decomposition		
91) $CH_3C(O)CH{=}CHCHO + OH \xrightarrow{O_2} H_2O + CH_3C(O)CH{=}CHC(O)O_2{\cdot}$	---	1.5×10^{-11}	---	1.5×10^{-11}	---	---	---	1.5×10^{-11}	---	cf. $OH + RCHO$ (A&L)		
92) $CH_3C(O)CH{=}CHCHO + OH \xrightarrow{O_2} CH_3C(O)CH(OH)C(O_2{\cdot})HCHO$	---	5.0×10^{-12}	---	5.0×10^{-12}	---	---	---	5.0×10^{-12}	-5.0×10^{2}	cf. $OH + {>}C{=}C{<}$ (A&L)		

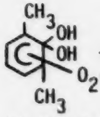
	Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
		(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
93)	$CH_3C(O)CH(OH)C(O_2\cdot)HCHO+$ $NO \xrightarrow{O_2} NO_2+HO_2+$ $CH_3C(O)CHO+(CHO)_2$		$6.8X10^{-12}$	---	$6.8X10^{-12}$	---	---	---	$6.8X10^{-12}$	$-1.8X10^2$	$C_5O_2+NO\rightarrow$ $RO+NO_2$	18	
94)	$CH_3C(O)CH=$ $CHC(O)O_2\cdot+$ $NO \xrightarrow{O_2} NO_2+CO_2$ $+CH_3C(O)CH=CHO_2\cdot$	---	$6.8X10^{-12}$	---	$6.8X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_5O_2+NO\rightarrow$ $RO+NO_2$	18	
95)	$CH_3C(O)CH=CHO_2\cdot+$ $NO \xrightarrow{O_2} NO_2 +$ $CH_3C(O)CH(O_2\cdot)CHO$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	$C_4O_2+NO\rightarrow$ $RO+NO_2$	18	
96)	$CH_3C(O)CH(O_2\cdot)CHO+$ $NO\rightarrow$ $CH_3C(O)CH(ONO_2)CHO$		$5.4X10^9$	---	$2.7X10^{-13}$	---	---	---	$5.6X10^{-13}$	$-1.8X10^2$	$C_4O_2+NO\rightarrow$ C_4ONO_2	18	
97)	$CH_3C(O)CH=$ $CHC(O)O_2\cdot+NO\rightarrow$ $CH_3C(O)CH=CHCO_3NO_2$	---	$4.7X10^{-12}$	---	$5.5X10^{-13}$	---	---	---	$9.6X10^{-12}$	---	---	13	

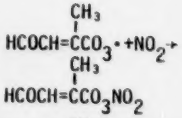
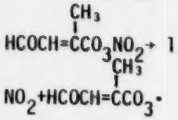
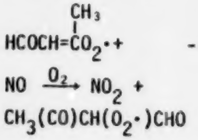
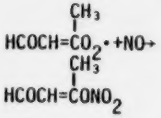
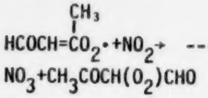
Reaction		L&S[1]	LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
98) $CH_3C(O)CH=CHCO_3NO_2 \rightarrow CH_3C(O)CH=CHC(O)O_2\cdot + NO_2$	---	$3.7X10^{-4}$ s^{-1}	---	$3.6X10^{-4}$ s^{-1}	---	---	---	$4.2X10^{-4}$	$1.333X10^{4}$	cf.PAN→ CH_3COO_2+ NO_2(CODATA [6])		
99) $CH_3C(O)CH(O_2\cdot)CHO + NO \xrightarrow{O_2} NO_2 + CH_3C(O)O_2\cdot + (CHO)_2$		$3.4X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^{2}$	C_4O_2+NO→ RO + NO_2	18	
100) $CH_3C(O)CH(O_2\cdot)CHO + NO \xrightarrow{O_2} NO_2 + HO_2 + CH_3C(O)CHO + CO$ alternative- $CH_3CO(O_2) + (CHO)_2$		$3.4X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^{2}$	C_4O_2+NO→ RO+NO_2	18	
101) $CH_3C(O)CH=CHO_2\cdot + NO \rightarrow CH_3C(O)CH=CHONO_2$	---	$5.4X10^{-13}$	---	$5.8X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	C_4O_2+NO→ C_4ONO_2	18	
102) $CH_3C(O)CH=CHO_2\cdot + NO_2 \xrightarrow{O_2} NO_3 + CH_3C(O)CH(O_2\cdot)CHO$	---	$6.8X10^{-12}$	---	$4.7X10^{-12}$	---	---	---	$6.0X10^{-12}$	---	via PAN decomposition	17	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
m-Xylene chemistry:												
103) 	---	$2.3X10^{-11}$	---	$2.4X10^{-11}$	---	---	---	$2.4X10^{-11}$	---	Exptl(A&L)	-	
104) 	$6.9X10^2$	$6.8X10^{-14}$	---	$7\ X10^{-15}$	---	---	---	$7\ X10^{-15}$	---	cf.RO+O_2→ >C=O+HO_2 (A&L)	-	
105) 	---	$3.2X10^{-14}$	---	$3.3X10^{-15}$	---	---	---	$3.3X10^{-15}$	---	See reaction(67) (discrepancy between L&S[1] and A&L[3])	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
106) 	---	$3.0X10^{-11}$	---	$3.1X10^{-11}$	---	---	---	$3.1X10^{-11}$	---	See reaction(66)	-	
107)  +NO→ NO_2+HO_2·+$CH_3C(O)CHO$ +0.5 $CH_3C(O)CH=CHCHO$ +0.5 $CH(O)CH=C(CH_3)CHO$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	RO_2+NO→ RO+NO_2	26	
108) 	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$2.8X10^{-11}$	---	---	14	

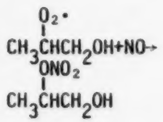
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
109) 	---	$1.5X10^{-11}$	---	$1.5X10^{-11}$	---	---	---	$1.5X10^{-11}$	---	cf.RO+ NO_2(A&L)		
110) 	---	$7.4X10^{-11}$	---	7 $X10^{-11}$	---	---	---	7 $X10^{-11}$	---	est. cf. OH+cresols	-	
111) 	---	$3.0X10^{-11}$	---	3 $X10^{-11}$	---	---	---	3 $X10^{-11}$	---	See reaction(66) (A&L)	-	
112) 		$3.2X10^{-14}$	---	$3.3X10^{-15}$	---	---	---	$3.3X10^{-15}$	---	See reaction(67) (A&L)	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
113)  +NO→ NO_2+HO_2+$CH_3COCOOH$+ 0.5 $CH_3COCH=CHCHO$+ 0.5 $CHOCH=C(CH_3)CHO$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	RO_2+NO→ RO_2+NO	26	
114) $CHOCH=C(CH_3)CHO$+ OH $\xrightarrow{O_2}$ $HCOC(OH)H\overset{O_2\cdot}{C}(CH_3)CHO$	---	$5.0X10^{-12}$	---	$5.0X10^{-12}$	---	---	---	$5X10^{-12}$	---	est. cf. OH+ $>C=C<$ (A&L)	-	
115) $HCOC(OH)H\overset{O_2\cdot}{C}(CH_3)CHO$+ NO $\xrightarrow{O_2}$ 0.88NO_2+ 0.88$(CHO)_2$+0.88$HO_2\cdot$+ CH_3COCHO+0.12$HCOC(OH)CH(ONO_2)(CH_3)CHO$		$6.8X10^{-12}$	---	$6.8X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	C_5O_2+ NO→RO+NO_2	18	
116) $CHOCH=C(CH_3)CHO$+ OH $\xrightarrow{O_2}$ $HCOCH=\overset{CH_3}{C}CO_3\cdot$+$H_2O$		$3.0X10^{-11}$	---	$3.0X10^{-11}$	---	---	---	$3.0X10^{-11}$	---	est.based on exptl data(A&L)	-	
117) $HCOCH=\overset{CH_3}{C}CO_3\cdot$+ NO $\xrightarrow{O_2}$ NO_2+$HCOCH=\overset{CH_3}{C}O_2\cdot$+$CO_2$	---	$6.8X10^{-12}$	---	$6.8X10^{-12}$	---	---	---	$1.0X10^{-11}$	---	---	13	

Reaction	L&S[1] (E/R)/K	L&S[1] k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)	LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work k	This Work (E/R)/K	Comments	Notes	References
118)  $HCOCH{=}\overset{CH_3}{C}CO_3{\cdot}+NO_2 \rightarrow HCOCH{=}\overset{CH_3}{C}CO_3NO_2$	---	$4.7X10^{-12}$	---	$4.7X10^{-12}$	---	---	---	$6.0X10^{-12}$	---	cf.CH_3COO_2+ NO_2→PAN (CODATA[6])		
119)  $HCOCH{=}\overset{CH_3}{C}CO_3NO_2 \rightarrow NO_2+HCOCH{=}\overset{CH_3}{C}CO_3{\cdot}$	$1.354X10^4$	$3.7X10^{-4}\ s^{-1}$	---	$3.6X10^{-4}$	---	---	---	$4.2X10^{-4}$	$1.333X10^4$	cf.PAN→ $CH_3COO_2+NO_2$	-	
120)  $HCOCH{=}\overset{CH_3}{C}O_2{\cdot}+NO \xrightarrow{O_2} NO_2 + CH_3(CO)CH(O_2{\cdot})CHO$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	$C_4O_2+NO \rightarrow RO+NO_2$	18	
121)  $HCOCH{=}\overset{CH_3}{C}O_2{\cdot}+NO \rightarrow HCOCH{=}\overset{CH_3}{C}ONO_2$	---	$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2+NO \rightarrow C_4ONO_2$	18	
122)  $HCOCH{=}\overset{CH_3}{C}O_2{\cdot}+NO_2 \rightarrow NO_3+CH_3COCH(O_2)CHO$	---	$6.8X10^{-12}$	---	$4.7X10^{-12}$	---	---	---	$6.8X10^{-12}$	---	via PAN decomposition	17	
123) $CH_3COCH(O_2)CHO+NO \rightarrow CH_3COCH(ONO_2)CHO$		$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2+NO \rightarrow C_4ONO_2$	18	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
124) $CH_3COCH(O_2)CHO+$ NO $\xrightarrow{O_2}0.93HO_2+0.1CO$ $+0.1CH_3COCHO$ $+0.07(CHO)_2$ $+0.83CH_3COCOCHO$ $+NO_2$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	$C_4O_2+NO\rightarrow$ $RO+NO_2$	18	
Ethene chemistry:												
125) $CH_2=CH_2+OH \xrightarrow{O_2}$ $HOCH_2CH_2O_2\cdot$	$-3.82X10^2$	$8.1X10^{-12}$	---	$8.1X10^{-12}$	---	$8.4X10^{-12}$	$8.5X10^{-12}$	$8.0X10^{-12}$	$-4.0X10^2$	NASA [5]	-	
126) $HOCH_2CH_2O_2\cdot+NO\rightarrow$ $NO_2+HOCH_2CH_2O\cdot$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_2O_2+NO\rightarrow$ $RO+NO_2$	18	
127) $HOCH_2CH_2O\cdot\rightarrow$ $HCHO+\cdot CH_2OH$	---	$9.3X10^4$ s^{-1}	---	$1.3X10^5$ s^{-1}	---	---	---	$1.1X10^5$ s^{-1}	$5.8X10^3$	A&L[3]	19b	
128) $HOCH_2CH_2O\cdot+O_2\rightarrow$ $HOCH_2CHO + HO_2\cdot$	$6.9X10^2$	$6.8X10^{-15}$	---	$6.9X10^{-15}$	---	---	---	$6.2X10^{-15}$	$7.1X10^2$	$\Delta H°=$ -32.7 kcal mol^{-1}	15	
129) $\cdot CH_2OH + O_2\rightarrow$ $HCHO + HO_2\cdot$	---	$2.0X10^{-12}$	---	$2.0X10^{-12}$	---	$2\ X10^{-12}$	$2\ X10^{-12}$	$2\ X10^{-12}$	---	CODATA[6]	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
130) $CH_2{=}CH_2+O_3 \xrightarrow{O_2}$ $HCHO+0.4\ \dot{C}H_2O\dot{O}+$ $0.18\ CO_2+$ $0.42CO+0.12H_2+$ $0.42H_2O+0.12\ HO_2\cdot$	2.56×10^{3}	1.7×10^{-18}	---	1.8×10^{-18}	---	---	---	1.8×10^{-18}	2.56×10^{3}	Product distribution according to A&L[3]	-	
Propene chemistry:												
131) $CH_3CHCH_2+OH \xrightarrow{O_2}$ $0.65\ CH_3\overset{O_2\cdot}{C}HCH_2OH+$ $0.35\ CH_3CH(OH)CH_2O_2\cdot$	-5.37×10^{2}	2.5×10^{-11}	---	2.5×10^{-11}	---	---	2.9×10^{-11}	2.9×10^{-11}	-5.4×10^{2}	CODATA[6] Note that E/R refers to 1 atm	-	
132) $CH_3\overset{O_2\cdot}{C}HCH_2OH+NO\rightarrow$ $NO_2+CH_3\overset{O\cdot}{C}HCH_2OH$	---	6.8×10^{-12}	---	7.3×10^{-12}	---	---	---	7.3×10^{-12}	-1.8×10^{2}	$C_3O_2+NO\rightarrow$ $RO + NO_2$	18	
133) $CH_3\overset{O\cdot}{C}HCH_2OH\rightarrow$ $CH_3CHO+\cdot CH_2OH$	---	$1.6\times10^{3}\ s^{-1}$	---	$1\ \times10^{5}\ s^{-1}$	---	---	---	1.1×10^{5}	5.8×10^{3}	---	19b	
134) $CH_3CH(OH)CH_2O\cdot\rightarrow$ $HCHO+CH_3\dot{C}HOH$	---	$1.7\ s^{-1}$	---	$1\ \times10^{5}\ s^{-1}$	---	---	---	1.1×10^{5}	5.8×10^{3}	---	19b	

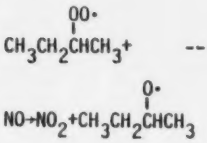
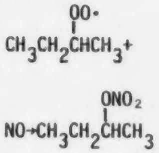
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
135)  $\overset{O_2\cdot}{CH_3CHCH_2OH}+NO\rightarrow\overset{ONO_2}{CH_3CHCH_2OH}$	---	$2.7X10^{-13}$	---	$2.9X10^{-13}$	---	---	---	$2.9X10^{-13}$	---	$C_3O_2+NO\rightarrow$ C_3ONO_2	18	
136) $CH_3CH(OH)CH_2O_2\cdot+NO\rightarrow NO_2+CH_3CH(OH)CH_2O\cdot$	---	$6.8X10^{-12}$	---	$7.3X10^{-12}$	---	---	---	$7.3X10^{-12}$	$-1.8X10^2$	$C_3O_2+NO\rightarrow$ $RO+NO_2$	18	
137) $CH_3CH(OH)CH_2O_2\cdot+NO\rightarrow CH_3CH(OH)CH_2ONO_2$	---	$2.7X10^{-13}$	---	$2.9X10^{-13}$	---	---	---	$2.9X10^{-13}$	---	$C_3O_2+NO\rightarrow$ C_3ONO_2	18	
138) $CH_3\dot{C}HOH+O_2\rightarrow HO_2\cdot+CH_3CHO$	---	$2.0X10^{-12}$	---	$2.0X10^{-12}$	---	---	---	$2.0X10^{-12}$	---	---	20	
139) $CH_3CHCH_2+O_3\rightarrow$ $0.5\ CH_3CHO+$ $0.2\ CH_3\dot{C}HO\dot{O}+$ $0.06\ CH_4+0.5\ CH_2O+$ $0.27\ CO_2+0.33\ CO+0.20\ HO_2\cdot$ $+0.1\ OH+0.22\ CH_3O_2\cdot$ $+0.03\ CH_3O\cdot+0.2\ \dot{C}H_2O\dot{O}$ $+0.06\ H_2+0.21\ H_2O$	$1.897X10^3$	$1.1X10^{-17}$	---	$1.1X10^{-17}$	---	---	---	$1.1X10^{-17}$	$1.897X10^3$	Product distribution according to A&L [3]	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
tr-2-butene chemistry:												
140) $CH_3CH{=}CHCH_3 + OH \xrightarrow{O_2} CH_3CH(OH)\overset{OO\cdot}{C}HCH_3$	$-5.42X10^2$	$6.8X10^{-11}$	---	$7.0X10^{-11}$	---	---	---	$7.0X10^{-11}$	$-5.42X10^2$	A&L [3]	-	
141) $CH_3CH(OH)\overset{OO\cdot}{C}HCH_3 + NO \rightarrow NO_2 + CH_3\overset{OH}{C}H\overset{O\cdot}{C}HCH_3$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	$C_4O_2 + NO \rightarrow RO + NO_2$	18	
142) $CH_3CH(OH)\overset{OO\cdot}{C}HCH_3 + NO \rightarrow CH_3\overset{OH}{C}H\overset{ONO_2}{C}HCH_3$	---	$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2 + NO \rightarrow C_4ONO_2$	18	
143) $CH_3CH(OH)\overset{O\cdot}{C}HCH_3 \rightarrow CH_3CHO + CH_3\dot{C}HOH$	---	$1.7X10^2\ s^{-1}$	---	$1\ \ X10^5\ s^{-1}$	---	---	---	$1.1X10^5\ s^{-1}$	$5.8X10^3$	---	19b	
144) $CH_3CH{=}CHCH_3 + O_3 \rightarrow CH_3CHO + 0.4\ CH_3\dot{C}HO\dot{O} + 0.12\ CH_4 + 0.36\ CO_2 + 0.24\ CO + 0.29\ HO_2\cdot + 0.19\ OH + 0.05\ CH_3O\cdot + 0.43\ CH_3O_2\cdot$	$1.051X10^3$	$1.8X10^{-16}$	---	$2.0X10^{-16}$	---	---	---	$2.0X10^{-16}$	$1.06X10^3$	Exptl data (A&L[3]) products according to A&L[3]		

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
145) $\dot{C}H_2O\dot{O}+NO\rightarrow NO_2+HCHO$	---	6.8×10^{-12}	---	$7\ \times10^{-12}$	---	---	---	$7\ \times10^{-12}$	-1.8×10^{2}	By analogy with $RO_2+NO\rightarrow RO+NO_2$	23	
146) $\dot{C}H_2O\dot{O}+NO_2\rightarrow NO_3+HCHO$	---	6.8×10^{-13}	---	$7\ \times10^{-13}$	---	---	---	$1\ \times10^{-13}$	---	---	23	
147) $\dot{C}H_2O\dot{O}+H_2O\rightarrow HCOOH+H_2O$	---	4.1×10^{-18}	---	$4\ \times10^{-18}$	---	---	---	$4\ \times10^{-16}$	---	---	23	
148) $CH_3\dot{C}HO\dot{O}+NO\rightarrow NO_2+CH_3CHO$	---	6.8×10^{-12}	---	$7\ \times10^{-12}$	---	---	---	$7\ \times10^{-12}$	-1.8×10^{2}	---	23	
149) $CH_3\dot{C}HO\dot{O}+NO_2\rightarrow NO_3+CH_3CHO$	---	6.8×10^{-13}	---	$7\ \times10^{-13}$	---	---	---	$1\ \times10^{-13}$	---	---	23	
150) $CH_3\dot{C}HO\dot{O}+H_2O\rightarrow CH_3COOH+H_2O$	---	4.1×10^{-18}	---	$4\ \times10^{-18}$	---	---	---	$4\ \times10^{-16}$	---	---	23	
Propane chemistry:												
151) $CH_3CH_2CH_3+OH\rightarrow H_2O+0.85\ CH_3\overset{OO\cdot}{C}HCH_3+0.15\ CH_3CH_2CH_2O_2\cdot$	6.8×10^{2}	1.6×10^{-12}	---	1.22×10^{-12}	---	1.1×10^{-12}	1.2×10^{-12}	1.2×10^{-12}	8.0×10^{2}	CODATA[6]	21	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
152) $CH_3\overset{OO\cdot}{C}HCH_3+NO\cdot\rightarrow$ $NO_2+CH_3\overset{O\cdot}{C}HCH_3$	---	$7.4X10^{-12}$	---	---	---	---	$7.6X10^{-12}$	$7.6X10^{-12}$	$-1.8X10^2$	$C_3O_2+NO\rightarrow$ $RO+NO_2$	18	
153) $CH_3CH_2CH_2O_2\cdot+NO\rightarrow$ $NO_2+CH_3CH_2CHO\cdot$	---	$7.4X10^{-12}$	---	---	---	---	$7.6X10^{-12}$	$7.6X10^{-12}$	$-1.8X10^2$	$C_3O_2+NO\rightarrow$ $RO+NO_2$	18	
154) $CH_3\overset{O\cdot}{C}HCH_3+O_2\rightarrow$ $HO_2\cdot+CH_3C(O)CH_3$	---	$3.0X10^{-14}$	---	$3\ X10^{-14}$ (Batt est.)	---	---	---	$1.4X10^{-14}$	$2.3X10^2$	$\Delta H°=-36.7$ kcal mol^{-1}	15	
155) $CH_3CH_2CH_2O\cdot+O_2\rightarrow$ $HO_2\cdot+CH_3CH_2CHO$	$6.9X10^2$	$6.8X10^{-14}$	---	---	---	---	---	$7.4X10^{-15}$	$6.5X10^2$	$\Delta H°=-33.0$ kcal mol^{-1}	15	
n-Butane chemistry:												
156) $CH_3CH_2CH_2CH_3+$ $O(^3P)\ \xrightarrow{O_2}$ $OH+0.88\ CH_3CH_2\overset{OO\cdot}{C}HCH_3$ $+0.12\ CH_3CH_2CH_2CH_2O_2\cdot$	$2.099X10^3$	$2.2X10^{-14}$	---	$2.2X10^{-14}$	---	---	---	$2.2X10^{-14}$	$2.1X10^3$	A&L[3], exptl data	-	

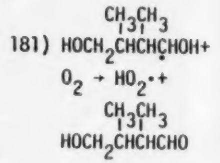
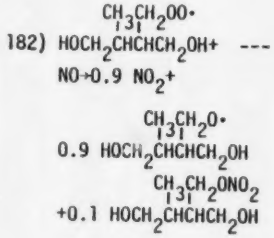
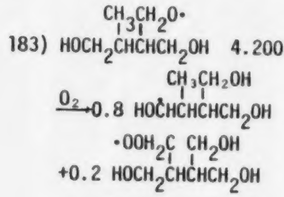
Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
157) $CH_3CH_2CH_2CH_3$+ OH $\xrightarrow{O_2}$ H_2O+ 0.86 $CH_3CH_2\overset{OO\cdot}{C}HCH_3$ +0.14 $CH_3CH_2CH_2CH_2O_2\cdot$	$5.59X10^2$	$2.6X10^{-12}$	---	$2.6X10^{-14}$	---	---	---	$2.6X10^{-12}$	$5.6X10^2$	A&L[3] exptl data	21	
158) $CH_3CH_2CH_2CH_2O_2\cdot$+ NO→$CH_3CH_2CH_2CH_2O\cdot$+NO_2	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^2$	C_4O_2+NO→ RO + NO_2	18	
159) $CH_3CH_2CH_2CH_2O_2\cdot$+ NO→$CH_3CH_2CH_2CH_2ONO_2$	$8.0X10^2$	$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	C_4O_2+NO→ C_4ONO_2	18	
160) $CH_3CH_2CH_2CH_2O\cdot$+ O_2→$HO_2\cdot$+ $CH_3CH_2CH_2CHO$	$6.90X10^2$	$6.8X10^{-15}$	---	7 $X10^{-15}$	---	---	---	$4.4X10^{-15}$	$8.1X10^2$	$\Delta H°=-31.7$ kcal mol^{-1}	15	
161) $CH_3CH_2CH_2CH_2O\cdot$ $\xrightarrow{O_2}$ $\cdot OOCH_2CH_2CH_2CH_2OH$	$4.200X10^3$	$1.2X10^5\ s^{-1}$	---	$1.1X10^5\ s^{-1}$	---	---	---	$5.7X10^5\ s^{-1}$	$3.9X10^3$	6R/3 prim(C-H)	22	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
162) $\cdot OOCH_2CH_2CH_2CH_2OH + NO \rightarrow NO_2 + \cdot OCH_2CH_2CH_2CH_2OH$		$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^{2}$	$C_4O_2 + NO \rightarrow RO + NO_2$	18	
163) $\cdot OOCH_2CH_2CH_2CH_2OH + NO \rightarrow O_2NOCH_2CH_2CH_2CH_2OH$		$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2 + NO \rightarrow C_4ONO_2$	18	
164) $\cdot OCH_2CH_2CH_2CH_2OH \rightarrow HOCH_2CH_2CH_2\dot{C}HOH$		$6.0X10^{5}\ s^{-1}$	---	$2\text{-}6X10^{5}\ s^{-1}$	---	---	---	$2.7X10^{6}$	$3.3X10^{3}$	6R/2 sec(C-H)	22	
165) $HOCH_2CH_2CH_2\dot{C}HOH + O_2 \rightarrow HO_2\cdot + OHCH_2CH_2CH_2CHO$	$6.90X10^{2}$	$6.8X10^{-15}$	---	2 $X10^{-12}$	---	---	---	2 $X10^{-12}$	---	---	20	
166)  $CH_3CH_2\overset{OO\cdot}{C}HCH_3 + NO \rightarrow NO_2 + CH_3CH_2\overset{O\cdot}{C}HCH_3$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	$-1.8X10^{2}$	$C_4O_2 + NO \rightarrow RO + NO_2$	18	
167)  $CH_3CH_2\overset{OO\cdot}{C}HCH_3 + NO \rightarrow CH_3CH_2\overset{ONO_2}{C}HCH_3$	---	$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2 + NO \rightarrow C_4ONO_2$	18	

Reaction	L&S[1] (E/R)/K	L&S[1]	LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work	This Work (E/R)/K	Comments	Notes	References
		k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)										
168) $CH_3CH_2\overset{O\cdot}{\overset{\vert}{C}}HCH_3 + O_2 \rightarrow CH_3CH_2C(O)CH_3 + HO_2\cdot$	---	3.0×10^{-14}	---	5×10^{-14}	---	---	---	2.2×10^{-14}	1.2×10^{2}	$\Delta H° = -37.9$ kcal mol⁻¹	15	
169) $CH_3CH_2\overset{O\cdot}{\overset{\vert}{C}}HCH_3 \xrightarrow{O_2} C_2H_5O_2\cdot + CH_3CHO$	7.0×10^{3}	6.7×10^{5} s⁻¹	---	5×10^{3}	---	---	---	1.8×10^{3}	7.5×10^{3}	$\Delta H° = 2.8$ kcal mol⁻¹ $\Delta S° = 34.6$ cal mol⁻¹K⁻¹	19a	
170) $C_2H_5O_2\cdot + NO \rightarrow C_2H_5O\cdot + NO_2$	---	7.4×10^{-12}	---	7.6×10^{-12}	---	---	$\pm 7.1 \times 10^{-12}$	7.6×10^{-12}	-1.8×10^{2}	cf. $CH_3O_2 + NO \rightarrow CH_3O + NO_2$		
171) $C_2H_5O\cdot + NO_2 \rightarrow C_2H_5ONO_2$	---	1.5×10^{-11}	---	1.5×10^{-11}	---	---	---	1.5×10^{-11}	---	cf. $CH_3O + NO_2 \rightarrow CH_3ONO_2$ Reaction (34)		
172) $C_2H_5O\cdot + NO \rightarrow C_2H_5ONO$	---	3.0×10^{-11}	---	---	---	---	---	---	---	not important		
173) $C_2H_5O\cdot + O_2 \rightarrow CH_3CHO + HO_2\cdot$	6.90×10^{2}	6.8×10^{-15}	---	7.0×10^{-15}	---	---	8×10^{-15}	7.4×10^{-15}	6.5×10^{2}	Exptl.	15	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
2,3-dimethyl butane chemistry:												
174) $(CH_3)_2$-$CHCH(CH_3)_2$+ $O(^3P)$→ $(CH_3)_2CHC(O_2\cdot)$- $(CH_3)_2$+OH	$1.250X10^3$	$2.1X10^{-13}$	---	$2.1X10^{-13}$	---	---	---	$2.1X10^{-13}$	$1.25X10^3$	Exptl (A&L[3])		
175) $(CH_3)_2CHCH(CH_3)_2$+ OH→ $0.14(CH_3)_2CHCH(CH_3)CH_2O_2\cdot$ $+0.86(CH_3)_2CHC(O_2\cdot)(CH_3)_2$	---	$6.3X10^{-12}$	---	$6.3X10^{-12}$	---	---	---	$6.3X10^{-12}$	$-1.29X10^2$	Exptl (A&L [3])	24	
176) $(CH_3)_2$- $CHCH(CH_3)CH_2O_2\cdot$+ NO→0.9 NO_2+ $0.9(CH_3)_2CHCH(CH_3)CH_2O\cdot$+ $0.1(CH_3)_2CHCH(CH_3)CH_2ONO_2$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	C_6O_2+NO→ RO+NO_2 C_6O_2+NO→ C_6ONO_2	18, 25	
177) $(CH_3)_2$- $CHCH(CH_3)CH_2O\cdot$+ O_2→$HO_2\cdot$+ $(CH_3)_2CHCH(CH_3)CHO$	$6.90X10^2$	$6.8X10^{-15}$	---	$6.9X10^{-15}$	---	---	---	$1.3X10^{-14}$	$4.9X10^2$	ΔH°=-34.6 kcal mol⁻¹	15	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
178) $(CH_3)_2CHCH-(CH_3)CH_2O\cdot \xrightarrow{O_2}$ $\cdot OOCH_2\overset{CH_3}{C}H\overset{CH_3}{C}HCH_2OH$	$4.20X10^3$	$2.3X10^5\ s^{-1}$	---	$2.2X10^5$	---	---	---	$5.7X10^5\ s^{-1}$	$3.9X10^3$	6R/3 primC-H	22	
179) $\cdot OOCH_2\overset{CH_3}{C}H\overset{CH_3}{C}HCH_2OH+$ $NO \rightarrow 0.9\ NO_2+$ $0.9\ \cdot OCH_2\overset{CH_3}{C}H\overset{CH_3}{C}HCH_2OH$ $+0.1\ O_2NOCH_2\underset{CH_3}{C}H\underset{CH_3}{C}HCH_2OH$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_6O_2+NO \xrightarrow{(a)}$ $RO+NO_2$ (b) $C_6O_2+NO \rightarrow$ C_6ONO_2 0.8(a) 0.2(b)	18	
180) $\cdot OCH_2-\overset{CH_3}{C}H\overset{CH_3}{C}HCH_2OH \xrightarrow{O_2}$ $0.8\ HOCH_2\overset{CH_3}{C}H\overset{CH_3}{C}HCHOH+$ $0.2\ HOCH_2\underset{CH_3}{C}H\underset{CH_2OO\cdot}{C}HCH_2OH$	$4.200X10^3$	$2.3X10^5\ s^{-1}$	---	$3.2X10^5\ s^{-1}$ (k_{a+b})		---	$k_a=2.7X10^6$ $k_b=5.4X10^5$	$3.2X10^6\ s^{-1}$	$3.3X10^3$	(a)6R/2 sec(C-H) (b)6R/3 prim(C-H)	22	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K		
181)  $HOCH_2\overset{CH_3}{C}H\overset{CH_3}{C}H\dot{C}HOH + O_2 \rightarrow HO_2\cdot + HOCH_2\overset{CH_3}{C}H\overset{CH_3}{C}HCHO$	$6.90X10^2$	$6.8X10^{-15}$	---	$2\ X10^{-12}$	---	---	---	$2\ X10^{-12}$	---	$R_1R_2CHOH + O_2 \rightarrow R_1R_2C=O + HO_2$	20
182)  $HOCH_2\overset{CH_3}{C}H\overset{CH_2OO\cdot}{C}HCH_2OH + NO \rightarrow 0.9\ NO_2 + 0.9\ HOCH_2\overset{CH_3}{C}H\overset{CH_2O\cdot}{C}HCH_2OH + 0.1\ HOCH_2\overset{CH_3}{C}H\overset{CH_2ONO_2}{C}HCH_2OH$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_6O_2+NO \xrightarrow{(a)} RO+NO_2$ $C_6O_2+NO \xrightarrow{(b)} C_6ONO_2$ 0.8(a) 0.2(b)	18
183)  $HOCH_2\overset{CH_3}{C}H\overset{CH_2O\cdot}{C}HCH_2OH \xrightarrow{O_2} 0.8\ HO\dot{C}H\overset{CH_3}{C}H\overset{CH_2OH}{C}HCH_2OH + 0.2\ HOCH_2\overset{\cdot OOH_2C}{C}H\overset{CH_2OH}{C}HCH_2OH$	$4.200X10^3$	$2.3X10^5\ s^{-1}$	---	$3.2X10^5\ s^{-1}$ (k_{a+b})	---	---	$k_a=2.7X10^6$ $k_b=5.4X10^5$	$3.2X10^6\ s^{-1}$	$3.3X10^3$	(a)6R/2 sec(C-H) (b)6R/3 prim(C-H)	22

Reaction	L&S[1] (E/R)/K	L&S[1] k	LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work k	This Work (E/R)/K	Comments	Notes	References
		k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)										
184) $HO\dot{C}H\overset{CH_3}{\overset{\vert}{C}}H\overset{CH_2OH}{\overset{\vert}{C}}HCH_2OH +$ $O_2 \rightarrow HO_2\cdot +$ $OHC\overset{CH_3}{\overset{\vert}{C}}H\overset{CH_2OH}{\overset{\vert}{C}}HCH_2OH$	$6.90X10^2$	$6.8X10^{-15}$	---	$2\ X10^{-12}$	---	---	---	$2\ X10^{-12}$	---	R_1R_2CHOH+ $O_2 \rightarrow R_1R_2C=O$ $+HO_2$	20	
185) $HOCH_2\overset{\cdot OOH_2C}{\overset{\vert}{C}}H\overset{CH_2OH}{\overset{\vert}{C}}HCH_2OH +$ $NO \xrightarrow{O_2} 0.9\ NO_2 +$ $0.9\ HO_2\cdot +$ $0.9(HOCH_2)_2CH\underset{CH_2OH}{\underset{\vert}{C}}HCHO$ $+\ 0.1\ HOCH_2\underset{O_2NOH_2C}{\underset{\vert}{C}}H\underset{CH_2OH}{\underset{\vert}{C}}HCH_2OH$	---	$6.8X10^{-15}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_6O_2+NO \xrightarrow{(a)}$ $RO + NO_2$ $C_6O_2+NO \xrightarrow{(b)}$ C_6ONO_2 0.8(a) 0.2(b)	18	
186) $(CH_3)_2CHC(O_2\cdot)$ $(CH_3)_2+NO\rightarrow$ $0.9\ NO_2+$ $0.9(CH_3)_2CHC(O\cdot)(CH_3)_2+$ $0.1(CH_3)_2CHC(ONO_2)(CH_3)_2$	---	$6.8X10^{-12}$	---	$7.6X10^{-12}$	---	---	---	$7.6X10^{-12}$	$-1.8X10^2$	$C_6O_2+NO \xrightarrow{(a)}$ $RO+NO_2$ $C_6O_2+NO \xrightarrow{(b)}$ C_6ONO_2 0.8(a) 0.2(b)	18	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
187) $(CH_3)_2CHC(O\cdot)-$ $(CH_3)_2 \xrightarrow{O_2}$ $CH_3C(O)CH_3+$ $CH_3CH(O_2\cdot)CH_3$	6.440×10^{3}	$5\ \times10^{5}\ s^{-1}$	---	$5.4\times10^{5}\ s^{-1}$	---	---	---	$1.0\times10^{4}\ s^{-1}$	6.6×10^{3}	ΔH°=0.6 kcal mol^{-1} ΔS°=35.2 cal $mol^{-1}K^{-1}$	19a	
188) $CH_3CH(O_2\cdot)CH_3+$ $NO\rightarrow CH_3CH(ONO_2)CH_3$	---	2.7×10^{-13}	---	2.9×10^{-13}	---	---	---	2.9×10^{-13}	---	$C_3O_2+NO\rightarrow$ C_3ONO_2	18	
189) $CH_3CH(O_2\cdot)CH_3+$ $NO\rightarrow NO_2+$ $CH_3CH(O\cdot)CH_3$	---	6.8×10^{-12}	---	7.3×10^{-12}	---	---	---	7.3×10^{-12}	-1.8×10^{2}	$C_3O_2+NO\rightarrow$ $RO + NO_2$	18	
Propionaldehyde chemistry:												
190) C_2H_5CHO+ $OH \xrightarrow{O_2} H_2O+$ $C_2H_5CO_3\cdot$	-2.5×10^{2}	1.9×10^{-11}	---	1.9×10^{-11}	---	---	---	1.9×10^{-11}	-2.5×10^{2}	A&L[3] Exptl.		
191) C_2H_5CHO+ $NO_3 \xrightarrow{O_2}$ $HNO_3+C_2H_5CO_3\cdot$	---	1.5×10^{-15}	---	1.4×10^{-15}	---	---	---	2.5×10^{-15}	---	As with CH_3CHO (corrected)	14	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
192) $C_2H_5CHO+h\nu \xrightarrow{O_2} C_2H_5O_2\cdot+HO_2\cdot+CO$	---	$8.4\times10^{-4}\ k_{NO_2}$	---	---	---	---	---	---	---	---	-	
193) $C_2H_5CO_3\cdot+NO_2\rightarrow C_2H_5CO_3NO_2$	---	4.7×10^{-12}	---	4.7×10^{-12}	---	---	---	$6\ \times10^{-12}$	---	cf. $CH_3COO_2+NO_2\rightarrow PAN$ CODATA[6]		
194) $C_2H_5CO_3\cdot+NO \xrightarrow{O_2} C_2H_5O_2\cdot+NO_2+CO$	---	7.4×10^{-12}	---	7.6×10^{-12}	---	---	---	$9.6\ \times10^{-12}$	---	cf. $CH_3COO_2+NO\rightarrow CH_3+CO_2+NO_2$ CODATA[6]		
195) $C_2H_5CO_3NO_2\rightarrow C_2H_5CO_3\cdot+NO_2$	1.354×10^{4}	$3.7\times10^{-4}\ s^{-1}$	---	$3.7\times10^{-4}\ s^{-1}$	---	---	---	$4.2\times10^{-4}\ s^{-1}$	1.333×10^{4}	cf. $PAN\rightarrow CH_3COO_2+NO_2$		
Butyraldehyde chemistry:												
196) $C_3H_7CHO+OH \xrightarrow{O_2} H_2O+C_3H_7CO_3\cdot$	---	2.5×10^{-11}	---	2.5×10^{-11}	---	---	---	2.5×10^{-11}	-2.5×10^{2}	A&L [3] Exptl.		
197) $C_3H_7CHO+NO_3 \xrightarrow{O_2} HNO_3+C_3H_7CO_3\cdot$	---	1.5×10^{-15}	---	1.5×10^{-15}	---	---	---	2.5×10^{-15}	---	As with CH_3CHO (corrected)	14	
198) $C_3H_7CHO+h\nu \xrightarrow{O_2} C_3H_7O_2\cdot+HO_2\cdot+CO$	---	$8.4\times10^{-4}k_{NO_2}$	---	---	---	---	---	---	---	---	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
199) $C_3H_7CO_3\cdot + NO_2 \rightarrow C_3H_7CO_3NO_2$	---	4.7×10^{-12}	---	4.7×10^{-12}	---	---	---	$6\ \times10^{-12}$	---	cf. $CH_3COO_2 + NO_2 \rightarrow PAN$ CODATA[6]		
200) $C_3H_7CO_3\cdot + NO \xrightarrow{O_2} NO_2 + CO_2 + C_3H_7O_2\cdot$	---	7.4×10^{-12}	---	7.6×10^{-12}	---	---	---	1.0×10^{-11}	---	cf. $CH_3COO_2 + NO \xrightarrow{O_2} RO_2 + CO_2 + NO_2$	13	
201) $C_3H_7CO_3NO_2 \rightarrow C_3H_7CO_3\cdot + NO_2$	1.354×10^{4}	$3.7\times10^{-4}\ s^{-1}$	---	$3.7\times10^{-4}\ s^{-1}$	---	---	---	$4.2\times10^{-4} s^{-1}$	1.333×10^{4}	cf. $PAN \rightarrow CH_3COO_2 + NO_2$ CODATA [6]		
202) $C_3H_7O_2\cdot + NO \rightarrow NO_2 + C_3H_7O\cdot$	---	7.4×10^{-12}	---	7.3×10^{-12}	---	---	---	7.3×10^{-12}	-1.8×10^{2}	$C_3O_2 + NO \rightarrow RO + NO_2$	18	
203) $C_3H_7O\cdot + NO \rightarrow C_3H_7ONO$	---	3.0×10^{-11}	---	---	---	---	---	---	---	not important		
204) $C_3H_7O\cdot + NO_2 \rightarrow C_3H_7ONO_2$	---	1.5×10^{-11}	---	?	---	---	---	1.5×10^{-11}	---	cf. $CH_3O + NO_2 \rightarrow CH_3ONO_2$ Reaction (34)		
Acetone chemistry:												
205) $CH_3C(O)CH_3 + OH \xrightarrow{O_2} H_2O + CH_3C(O)CH_2O_2\cdot$	1.230×10^{3}	2.8×10^{-13}	---	2.8×10^{-13}	---	---	---	2.8×10^{-13}	1.23×10^{3}	A&L[3] est. by cf. $CH_3COCOCH_3$ and C_2H_6		

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
206) $CH_3C(O)CH_3 + h\nu \xrightarrow{O_2} CH_3CO_3\cdot + CH_3O_2\cdot$	---	$1.7\times10^{-4} k_{NO_2}$	---	---	---	---	---	---	---	---	-	
207) $CH_3C(O)CH_2O_2\cdot + NO \rightarrow CH_3C(O)CH_2O\cdot + NO_2$	---	6.8×10^{-12}	---	7.3×10^{-12}	---	---	---	7.3×10^{-12}	-1.8×10^{2}	$C_3O_2 + NO \rightarrow RO + NO_2$	18	
208) $CH_3C(O)CH_2O_2\cdot + NO \rightarrow CH_3C(O)CH_2ONO_2$	---	2.7×10^{-13}	---	2.8×10^{-13}	---	---	---	2.9×10^{-13}	---	$C_3O_2 + NO \rightarrow C_3ONO_2$	18	
209) $CH_3C(O)CH_2O\cdot + O_2 \rightarrow HO_2\cdot + CH_3C(O)CHO$	6.9×10^{2}	6.8×10^{-15}	---	7.3×10^{-15}	---	---	$k(O_2) = 3.6\times10^{3}\ s^{-1}$	6.9×10^{-16}	1.4×10^{3}	$\Delta H° = -26.8$ kcal mol⁻¹	15	
$CH_3C(O)CH_2O \rightarrow CH_3\dot{C}O + HCHO$	---	---	---	---	---	---	---	$6.4\times10^{2} s^{-1}$	7.8×10^{3}	$\Delta H° = 3.7$ kcal mol⁻¹ $\Delta S° = 35.0$ cal mol⁻¹K⁻¹	19a	
210) $C_2H_5C(O)CH_3 + OH \xrightarrow{O_2} H_2O + \overset{OO\cdot}{\overset{\vert}{CH_3CH}}C(O)CH_3$	---	5.5×10^{-13}	---	5.5×10^{-13}	---	---	---	5.5×10^{-13}	---	A&L[3], Exptl	19a	
211) $C_2H_5C(O)CH_3 + h\nu \xrightarrow{O_2} CH_3CO_3\cdot + C_2H_5O_2\cdot$		$1.7\times10^{-3} k_{NO_2}$	---	---	---	---	---	---	---	---	-	

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K		
212) $C_2H_5C(O)CH_3+$ $OH \xrightarrow{O_2} H_2O+$ $C_2H_5C(O)CH_2O_2\cdot$	---	$3.3X10^{-13}$	---	$3.3X10^{-13}$	---	---	---	$3.3X10^{-13}$	---	A&L[3] Exptl.	-
213) $CH_3\overset{OO\cdot}{C}HC(O)CH_3+$ $NO \rightarrow NO_2+$ $CH_3\overset{O\cdot}{C}HCOCH_3$	---	$6.8X10^{-12}$	---	$7.0X10^{-12}$	---	---	---	$7.0X10^{-12}$	---	$C_4O_2+NO\rightarrow$ $RO + NO_2$	18
214) $CH_3\overset{OO\cdot}{C}HC(O)CH_3+$ $NO \rightarrow CH_3\overset{ONO_2}{C}HC(O)CH_3$	---	$5.4X10^{-13}$	---	$5.6X10^{-13}$	---	---	---	$5.6X10^{-13}$	---	$C_4O_2+NO\rightarrow$ C_4ONO_2	18
215) $CH_3\overset{O\cdot}{C}HC(O)CH_3$ $\xrightarrow{O_2} CH_3CHO+CH_3CO_3\cdot$	$6.440X10^3$	$1.3X10^5$ s^{-1}	---	$1.3X10^5$	---	---	---	$1.6X10^5$ s^{-1}	$6.4X10^3$	$\Delta H°=-1.5$ kcal mol^{-1} $\Delta S°=37.2$ cal $mol^{-1}K^{-1}$	19a
216) $CH_3CH(O)COCH_3+$ $O_2\rightarrow$ $CH_3COCOCH_3+HO_2$	---	---	---	$3X10^{-14}$	---	---	---	$2.2X10^{-15}$	$8.1X10^2$	$\Delta H°=-31.7$ kcal mol^{-1}	15

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule⁻¹ s⁻¹ (298K 1 atm air)							(E/R)/K			
217) $C_2H_5C(O)CH_2O_2$+ NO→NO_2+ $C_2H_5C(O)CH_2O$	---	---	---	---	---	---	---	$7.0X10^{-12}$	$-1.8X10^{2}$	C_4O_2+NO→ RO+NO_2	18	
218) $C_2H_5C(O)CH_2O_2$+ NO→$C_2H_5C(O)CH_2ONO_2$	---	---	---	---	---	---	---	$5.6X10^{-13}$	---	C_4O_2+NO→ C_4ONO_2	18	
219) $C_2H_5C(O)CH_2\dot{O}$+ O_2→C_2H_5COCHO+ HO_2	---	---	---	---	---	---	---	$6.9X10^{-16}$	$1.4X10^{3}$	ΔH°=-26.8 kcal mol^{-1}	15	
220) $C_2H_5C(O)CH_2\dot{O}$ $\xrightarrow{O_2}$$C_2H_5CO_3$+ CH_2O	---	---	---	---	---	---	---	$6.4X10^{2}s^{-1}$	$7.8X10^{3}$	ΔH°=3.7 kcal mol^{-1} ΔS°=35.0 cal $mol^{-1}K^{-1}$	19a	
Additional Inorganic Reactions:												
a) NO_2+O_3→NO+2O_2	---	---	---	---	---	---	---	$9.7X10^{-19}$	---	---	4	Cantrell et al.[10]
b) NO_3+M→NO+O_2+M	---	---	---	---	---	---	---	$1.2X10^{-22}$	$6.84X10^{3}$	---	5	Cantrell et al.[10]
c) NO_3+HO_2→$HONO_2$+O_2	---	---	---	---	---	---	---	$2.5\pm1.5X10^{-12}$	---	---	6	Cantrell et al.[10]
d) OH+HONO→H_2O+NO_2	---	---	---	$6.6X10^{-12}$	$6.6X10^{-12}$	---	---	$6.6X10^{-12}$	---	---	7	Cox et al. [11]

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm^3 molecule^{-1} s^{-1} (298K 1 atm air)							(E/R)/K			
Additional Inorganic Reactions (continued):												
e) $OH+HONO_2 \rightarrow H_2O+NO_3$	---	---	$1.3X10^{-13}$	$1.3X10^{-13}$	---	$1.3X10^{-13}$	$1.3X10^{-13}$	$1.3X10^{-13}$	$-7.78X10^2$	NASA[5]	-	
f) $OH+HO_2NO_2 \rightarrow H_2O+O_2+NO_2$	---	---	$4\ X10^{-12}$	---	---	$4.6X10^{-12}$	$4.6X10^{-12}$	$4.6X10^{-12}$	$-3.8X10^2$	NASA[5]	-	
g) $OH+NH_3 \rightarrow H_2O+NH_2$	---	---	---	---	---	$1.6X10^{-13}$	$1.6X10^{-13}$	$1.6X10^{-13}$	$9.0X10^2$	NASA[5]	-	
h) $NH_2+NO \rightarrow N_2+H_2O$	---	---	---	---	---	$1.6X10^{-11}$	$1.6X10^{-11}$	$1.6X10^{-11}$	$-4.5X10^2$	NASA[5]	-	
i) $NH_2+NO_2 \rightarrow N_2O+H_2O$	---	---	---	---	---	$1.7X10^{-11}$	$1.7X10^{-11}$	$1.7X10^{-11}$	$-6.5X10^2$	NASA[5]	-	
j) $NH_2+O_3 \rightarrow NH_2O+O_2$	---	---	---	---	---	$1.2X10^{-13}$	$1.2X10^{-13}$	$3.3X10^{-13}$	$1.15X10^3$	---	-	Patrick&Golden[36]
k) $NH_2O+O_2 \rightarrow HNO+HO_2$	---	---	---	---	---	---	---	$1.0X10^{-14}$	$2.9X10^3$	---	8	
l) $HO+SO_2+M \rightarrow HOSO_2+M$	---	---	$9X10^{-13}$	---	---	$1.1X10^{-12}$	$1.1X10^{-12}$	$1.1X10^{-12}$	see note	---	9	Calvert _et_ _al_.[12]
m) $HOSO_2 \xrightarrow[H_2O]{O_2} H_2SO_4+HO_2$	---	---	---	---	---	---	---	$(4\pm2)X10^{-13}$	?	---	-	Margitan[13]
n) $O(^3P)+SO_2+M \rightarrow SO_3+M$	---	---	---	$3.3X10^{-14}$	---	---	$3.4X10^{-14}$	$3.4X10^{-14}$	$1.0X10^3$	CODATA[6]	10	
o) $O_2(^1\Delta_g)+SO_2 \rightarrow$ products		---	---	---	---	---	---	$3.9X10^{-20}$	---	---	10	Calvert&Stockwell[14]
p) $O_2(^1\Sigma_g)+SO_2 \rightarrow$ products		---	---	---	---	---	---	$6.6X10^{-16}$	---	---	10	Calvert&Stockwell[14]

Reaction	L&S[1]		LLA[2]	A&L[3]	WKJ[4]	NASA[5]	CODATA[6]	This Work		Comments	Notes	References
	(E/R)/K	k/cm³ molecule^{-1} s^{-1} (298K 1 atm air)							(E/R)/K			
Additional Inorganic Reactions (continued):												
q) $O_3+SO_2 \rightarrow O_2+SO_3$	---	---	---	---	---	---	---	$<8X10^{-24}$	---	---	10	
r) $OH + H_2S \rightarrow$ Products	---	---	---	---	---	$4.7X10^{-12}$	$4.8X10^{-12}$	$4.7X10^{-12}$	$6.5X10^{1}$	NASA[5]	-	
s) $OH+CH_3SCH_3 \rightarrow$ Products	---	---	---	---	---	---	$7.8X10^{-12}$	$7.8X10^{-12}$	---	CODATA[6]	-	
t) $O+NO_2+M \rightarrow NO_3+M$	---	---	---	---	---	$1.6X10^{-12}$	$1.8X10^{-12}$	$1.8X10^{-12}$	$-4.2X10^{2}$	CODATA[6]	-	

NOTES TO TABLE I

1. The CODATA evaluation [6] of this rate constant differs slightly from the NASA No. 6 recommendation [5] which is $k = 1.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for 1 atm of air. We have selected the former evaluation to be consistent with the data for the reverse reaction, $HO_2NO_2 \rightarrow HO_2 + NO_2$, for which there is no NASA recommendation.

2. This rate constant is the sum of two separate expressions for the reactions:

$$HO_2 + HO_2 \xrightarrow{(1)} H_2O_2 + O_2$$

$$HO_2 + HO_2 + M \xrightarrow{(2)} H_2O_2 + O_2 + M$$

i.e., $k_1 = 2.2 \times 10^{-13} \exp(+620/T)$ cm^3 molecule^{-1} s^{-1}, and $k_2 = 1.9 \times 10^{-33}$ [M] $\exp(+980/T)$ cm^3 molecule^{-1} s^{-1}.

Thus at 298 K and 1 atm pressure

$$k = k_1 + k_2 = 1.7 \times 10^{-12} + 5 \times 10^{-32} [M]$$
$$= 2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The water vapor dependence of the rate constant is calculated from the empirical expression of Sander _et_ _al_. [7]:

$$k_{overall} = k(1 + 1.4 \times 10^{-21} \exp(2200/T) [H_2O]) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

2a. For the reaction

$$O(^1D) + M \xrightarrow{(1)} O(^3P) + M$$

L&S [1], LLA [2], A&L [3] and WKJ [4] have all taken $k_1 = 2.9 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for M = air, computed from $k_{O_2} = 4.0 \times 10^{-11}$ and $k_{N_2} = 2.6 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} as recommended both by NASA [5] and CODATA [6].

3. The older equilibrium constant estimates for the reactions, $N_2O_5 <=> NO_2 + NO_3$, of Schott and Davidson [39] and Graham and Johnston [40] have been questioned by the recent results of Tuazon et al. [41]. A more recent direct study of the equilibrium near 25°C by Perner et al. [42] give results which are in accord with the Graham and Johnston estimates, and the present rate constant choices for the forward and reverse reactions of this equilibrium have been made consistent with the Johnston and Graham data and the Malko and Troe [43] and Johnston et al. [44] re-evaluations of the kinetic data.

4. This reaction was suggested by Graham and Johnston (J. Phys. Chem., 60, 4628 (1974), 82, 254 (1978)) and by Wu, Morris and Niki (J. Phys. Chem., 77, 2507 (1973)) to explain the observed stoichiometry of the NO_2-O_3 reaction. This stoichiometry, $\Delta NO_2/\Delta O_3 < 2$ has recently been confirmed by Cox and Coker (J. Atmos. Chem., 1, 53 (1983)) and by Cantrell et al. [10]. The selected rate constant is that calculated by Cantrell et al. [10] and Johnston et al. [44] to computer fit their $\Delta NO_2/\Delta O_3$ measurements in several kinetic studies of the NO_3-CH_2O reaction.

5. This reaction has been suggested in a recent review by Johnston et al. [44] to rationalize both the high temperature decomposition of NO_3 observed by Schott and Davidson [39] and the room temperature experiments of Graham and Johnston [40], Tuazon et al. [41] and Cantrell et al. [10].

6. This reaction was found to be necessary in the study of the NO_3-CH_2O reaction by Cantrell et al. [10], in order to match the $[NO_3]$ and $[O_3]$ decay curves. The recommended rate constant, with its associated error limits, is from a computer simulation of the NO_3-CH_2O reaction system [10].

7. This result is based on the data of Cox, Derwent and Holt [11] from the photolysis of HONO in synthetic air plus NO and NO_2 at 1 atm pressure and 298 K, explained by the mechanism:

$$\mathrm{HONO + h\nu \rightarrow OH + NO}$$
$$\mathrm{OH + NO + M \xrightarrow{k_1} HONO + M}$$
$$\mathrm{OH + NO_2 + M \xrightarrow{k_2} HONO_2 + M}$$
$$\mathrm{OH + HONO \xrightarrow{k_3} H_2O + NO}$$

From experiments in the presence of H_2, the authors derived →

$k_x/k_{11} = 996 \pm 51$ where k_{11} refers to

$$\mathrm{OH + H_2 \xrightarrow{k_{11}} H_2O + H}$$

and $k_x = f_1k_1 + f_2k_2 + f_3k_3$ with f_1, f_2 and f_3 the fractions of NO, NO_2 and HONO making up the NO_x. The original authors assumed that $k_1 = k_2$ and took a value of $k_{11} = 7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} to derive $k_3 = 6.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. A recalculation taking the NASA [5] recommendations $k_1 = 4.8 \times 10^{-12}$ and $k_2 = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (1 atm air at 298 K) and the CODATA [6] value of $k_{11} = 6.7 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} yields the same value of $k_3 = 6.6 \times 10^{-12}$. A worrying feature of these experiments [11] is that the experimental ratio of $k_2/k_1 = 0.61$ was obtained, whereas the NASA No. 6 [5] recommended rate constants yield $k_2/k_1 = 2.3$. A value of $k_2/k_1 > 1$ would be expected on theoretical grounds based on the molecular complexities of the two reactions.

8. The rate constant, $k = 1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} is estimated from $\Delta H° \simeq -13$ kcal mol^{-1}, on the basis that for the reaction $CH_3O + O_2 \rightarrow CH_2O + HO_2$, $k = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and $\Delta H° = -27$ kcal mol^{-1}, $E = 5.7$ kcal mol^{-1}.

9. The second-order rate constant (k^{II}) has been calculated from the empirical expression $\ln(1/k^{II}) = 110.7758 + 3.1953 \ln(1/[M]) + 2.9808 \times 10^{-2} (\ln(1/[M]))^2$ derived from a fit of the most recent reliable experimental data [12]. This expression yields a value of k^{II} in excellent agreement with the most recent NASA [5] and CODATA [6] evaluations.

   The temperature coefficient of k^{II}, which is a function of the total pressure, has been calculated for the temperature range 200-300 K by taking an average of the temperature coefficients recommended by NASA [5] and CODATA [6], which is fitted by the expression: $-(E/R)/K = 3.6896 \times 10^{-4} (P/Torr)^2 - 6.793 \times 10^{-1} (P/Torr) + 5.3374 \times 10^2$.

10. These reactions were considered by Calvert and Stockwell [13] and from their rate constants, coupled with the estimated atmospheric concentrations of the reactants, it was concluded that they are unimportant in the SO_2 gas-phase oxidation in the troposphere. It should be noted, however, that under certain atmospheric conditions, e.g., in the early stages of stack gas dilution in air, the $O(^3P) + SO_2$ reaction can provide rather high instantaneous rates of SO_2 oxidation, which fall quickly with dilution.

11. The Atkinson and Lloyd [3] recommendation is based on experimental data for the ratio of rate constants k_1/k_2,

$$RO + NO \xrightarrow{(1)} RONO$$

$$RO + NO_2 \xrightarrow{(2)} RONO_2$$

where the experimental data are consistent with $k_1/k_2 = 2 \pm 1$ independent of the alkoxy radical RO.

Hence taking $k_1 = 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (based on data for the reverse decompositions of nitrates and equilibrium constants) it follows that $k_2 = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. Note that the recent direct studies:

$CH_3O + NO \rightarrow$ products, $k = 2.08 \times 10^{-11}$
(Sanders et al., Chem. Phys.Lett., 48, 203 (1980))

$CH_3O + NO_2 \rightarrow$ products, $k = 1.68 \times 10^{-12}$
(Jeffries et al., Chem. Phys. Lett., 106, 111 (1984))

both involve low pressure systems, and the measured rate constants are probably in the fall-off region.

12. There are currently two experimental estimates of the rate constant for the reaction, $HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$. From molecular modulation spectrometry, CH_3O_2 and HO_2 were monitored directly by Cox and Tyndall [46] in a Cl_2, CH_4, H_2, O_2 photochemical system. They reported $k = 7.7(+18.4$ or $-5.4) \times 10^{-14} \exp(1296 \pm 364)/T$ cm^3 molec^{-1} s^{-1} over the range 275-338 K. At 298 K this gives $k = 6.0 \times 10^{-12}$, or the very wide range of values, 6.9×10^{-11} to 5.2×10^{-13} cm^3 molec^{-1} s^{-1} with their stated uncertainty limits. In experiments of Kan et al. [47] at 298 K a value of 1.3×10^{-12} cm^3 molec^{-1} s^{-1}

was derived from the computer simulation of the product rates determined using Fourier transform infrared analysis in the photo-oxidation of azomethane in varied amounts of oxygen gas. The Kan et al. values depend on the measured rates of CH_3O_2H and other products of the reactions and the choice for the rate constants k_a and k_b for the reactions: $2HO_2 \rightarrow H_2O_2 + O_2$ (a) and $2CH_3O_2 \rightarrow$ Products (b). k_a and k_b appear to be reasonably well established; see note 2, and the discussion of Atkinson and Lloyd related to k_b [3]. Application of the approximate geometric mean rule, $k_{ab} = 2(k_a\ k_b)^{1/2}$, gives for the rate constant of the $CH_3O_2 + HO_2$ reaction, $k = 2.0 \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, in fair agreement with the estimate of Kan et al. [47]. Niki et al. [48] estimated the rate constant, $k_c = 1.5\ (\pm\ 0.5) \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1} for the analogous reaction, $C_2H_5O_2 + HO_2 \rightarrow C_2H_5O_2H + O_2$ (c). On the basis of the current information on the HO_2-RO_2 reactions we have adopted a value of 1.5×10^{-12} cm^3 $molec^{-1}$ s^{-1}, independent of temperature, for all the RO_2-HO_2 reactions. This lies within the uncertainty limits of all of the determinations, but obviously a very high uncertainty is associated with these rate constants.

13. Our evaluation is based on the same data as used in the CODATA [6] evaluation but with a modified interpretation. Thus, for the reactions

$$CH_3COO_2 + NO \xrightarrow{(1)} CH_3 + CO_2 + NO_2$$

$$CH_3COO_2 + NO_2 \xrightarrow{(2)} CH_3COO_2NO_2$$

We have taken k_1/k_2 = 1.7, the average of the experimental data of Cox et al. (J. Chem. Soc. Faraday Trans. I, 72, 2061 (1976)) and of Cox and Roffey (Environ. Sci. Technol., 11, 900 (1977)) and have rejected the value k_1/k_2 = 3.5 of Hendry and Kenley (J. Amer. Chem. Soc., 99, 3198 (1977)). Hence from $k_2 = 6 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} (Addison et al., Chem. Phys. Lett., 73, 283 (1980)), we deduce that $k_1 = 1.0 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}.

14. The rate constant choice given here is based upon the recent kinetic data of Cantrell et al. [10]. The recently published lower estimates of this constant (factor of 1/1.8) by Atkinson et al. [45], become consistent with the rate constant choice made here if the equilibrium constant for the reactions, $N_2O_5 <=> NO_2 + NO_3$, determined by the same group (Tuazon et al. [41]) is used together with their kinetic data. As Tuazon et al. [41] suggest, the use of their measured equilibrium constant raises by a factor of 1.84 all of the values of the NO_3-RH rate constants which they have published recently. The possible origins of these differences has been discussed by Cantrell et al. [10]. In the present study the rate constant for all of the other NO_3 reactions with various organic reactants reported by the Pitts research group have been raised by the 1.84 factor as well. For all C_2 and higher aldehydes, we have used the corrected value for CH_3CHO ($k = 2.5 \times 10^{-15}$ cm^3 $molec^{-1}$ s^{-1}). See the discussion of these reactions in the text.

15. Experimental data for this important class of reaction are available only for the reactions

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad (1)$$

$$C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2 \qquad (2)$$

Thus Gutman, Sanders and Butler [15] report $k_1 = 1.05 \times 10^{-13}$ $\exp(-1310/T)$ and $k_2 = 7.0 \times 10^{-14} \exp(-650/T)$ but note that for reaction (2) data were obtained at temperatures of 296 and 353 K and that the A-factor is chosen to fit the more extensive data for reaction (1).

The above results have been taken as the basis for estimating rate constants for this type of reaction, i.e.,

$$RO + O_2 \rightarrow \text{carbonyl compound} + HO_2$$

according to a procedure described by Baldwin et al. [16]. This consists of estimating A and E separately. Thus, based on the data for reaction (1), the A-factor is taken to be $3.5 \times 10^{-14} \times n$, where n is the number of H atoms in the radical capable of reaction to give the carbonyl product.

The activation energy is estimated from the enthalpy change for the particular reaction. For reactions (1) and (2) above, we have

	$CH_3O + O_2 \rightarrow$	CH_2O	+	HO_2	
ΔH_f°	3.8[17]	-25.95 [18]		2.5 [19]	$\Delta H^\circ = -27.25$
	$C_2H_5O + O_2 \rightarrow$	CH_3CHO	+	HO_2	
ΔH_f°	-4.1 [20]	-39.73 [18]		2.5 [19]	$\Delta H^\circ = -33.13$

Assuming that the experimental activation energies $E_1 = 2.6$ and $E_2 = 1.3$ kcal mol^{-1} are directly related to the enthalpy changes, it can be shown that

$$E = 8.62 + 0.221\ \Delta H$$

Gutman, Sanders and Butler [15] derived the equation

$$E = 12.63 + 0.34\ \Delta H$$

but the sources of their thermochemical data to obtain ΔH are not clearly stated.

For the reaction

$$C_6H_5CH_2O + O_2 \rightarrow C_6H_5CHO + HO_2$$

$\Delta H = -34.2$ kcal mol^{-1}, thus $E = 1.1$ kcal mol^{-1} and $A = 3.5 \times 10^{-14} \times 2 = 7.0 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. It follows that $k_{298} = 1.1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

The sources of thermochemical data used to calculate the ΔH values are as follows:

(a) for molecules- Cox and Pilcher [18] and Benson [21]

(b) for radicals - Benson [21], Kerr [22] and O'Neal and Benson [23]

16. Data derived from a least-mean-squares treatment of the rate constants of Ohta and Mizoguchi [24] and of Kenley and Hendry [25] for experiments with added NO and corrected for decomposition of BzPN at the walls of the reaction vessel.

17. Here we follow the recommendation of A and L [3] in assuming that the reaction proceeds via the formation of the peroxy nitrates

followed by the decomposition to give a resonance stabilized alkoxy radical + NO_3:

$$C_6H_5O_2 + NO_2 \rightarrow C_6H_5OONO_2$$

$$C_6H_5OONO_2 \rightarrow C_6H_5O + NO_3$$

The same possibility exists for vinyl peroxy radicals:

$$RCH{=}CHO_2 + NO_2 \rightarrow RCH{=}CHOONO_2$$

$$RCH{=}CHOONO_2 \rightarrow \underset{R\dot{C}HCHO}{\underset{\updownarrow}{RCH{=}CH\dot{O}}} + NO_3$$

These alternative modes of decomposition of phenyl and vinyl peroxy nitrates have been proposed by Hendry and Kenley [17] on thermochemical grounds, but, as yet, there are no experimental data to test this hypothesis.

In this sequence of reactions the rate controlling step will be the rate of formation of the peroxy nitrates.

18. Carter, Atkinson and coworkers [27-30] have established that the reaction of RO_2 with NO involves a second channel to produce an alkylnitrate, i.e.:

$$RO_2 + NO \xrightarrow{(a)} RO + NO_2$$

and $$RO_2 + NO \xrightarrow{(b)} RONO_2$$

Evidence for reaction (b) also comes from smog chamber studies carried out by Hoshino _et al_. [31] and by Takagi _et al_. [32].

Rate contant ratios (k_b/k_a) derived by these workers for various alkylperoxy radicals (RO_2) are summarized below along with the derived rounded-off ratios which we have used to calculate the fractions of reactions yielding the nitrate products.

Radical (R)	k_b/k_a* exptl	Reference	Radical Type	k_b/k_a
C_2H_5	≤0.014	[29]	C_2	0
C_3H_7	0.036	[29]	C_3	0.04
C_4H_9	0.077	[29]	C_4	0.08
C_5H_{11}	0.117	[29]	C_5	0.12
C_6H_{13}	0.208	[29]	C_6	0.21
C_7H_{15}	0.293	[29]	C_7	0.29
C_8H_{17}	0.318	[29]	C_8	0.32
cyclo-C_5H_9	0.045	[32]	cyclo C_5-C_7	0.06
cyclo-C_6H_{11}	0.090	[32]		
cyclo-C_7H_{13}	0.050	[32]		
$C_6H_5CH_2$	≤0.12	[31]		

*Data refer to room temperature and 1 atm pressure.

Based on the direct study of the reaction

$$CH_3O_2 + NO \rightarrow CH_3\dot{O} + NO_2$$

for which it has been shown [5,6] that $k = 4.2 \times 10^{-12} \exp(180/T)$; i.e., $k_{298} = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, we have followed the recommendation of Atkinson and Lloyd [3] and assumed that for all RO_2 radicals $k_a + k_b = 4.2 \times 10^{-12} \exp(180/T)$;

i.e., $k_{298} = 7.6 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The separate k_a and k_b values for the various C_3-C_8 radicals are then calculated from the previous k_b/k_a ratios:

	298 K	
Radical Type	k_a/cm^3 molecule^{-1} s^{-1}	k_b/cm^3 molecule^{-1} s^{-1}
C_3	7.3×10^{-12}	2.9×10^{-13}
C_4	7.0×10^{-12}	5.6×10^{-13}
C_5	6.8×10^{-12}	8.2×10^{-13}
C_6	6.3×10^{-12}	1.3×10^{-12}
C_7	5.9×10^{-12}	1.7×10^{-12}
C_8	5.8×10^{-12}	1.8×10^{-12}
cyclo-C_6-C_7	7.2×10^{-12}	4.5×10^{-13}

Atkinson and coworkers [30] have studied the effects of temperature and pressure upon the ratio k_b/k_a for C_5 and C_7 alkyl radicals. The alkyl nitrate yields were found to be markedly temperature and pressure dependent. Thus, k_b/k_a increased with increasing pressure and with decreasing temperature. The mechanism proposed by Atkinson and coworkers to explain the formation of the nitrates involves the chemically activated molecule $ROONO^*$ which isomerizes to $RONO_2$. As the authors pointed out, however, the relatively large temperature dependence of k_b/k_a is inconsistent with a purely chemical activation mechanism.

In view of the difficulties involved in explaining the effect of temperature upon the observed ratio of rate constants k_b/k_a we have chosen to ignore both pressure and temperature effects upon the formation of the nitrates in these RO_2 + NO reactions, until the mechanism of these interesting reactions is defined better.

19a. We have calculated the rate parameters for the alkoxy radical decomposition reactions, RO → carbonyl compound + alkyl radical, according to the procedures described by Baldwin et al. [16].

The activation energies (E) are calculated from the enthalpy changes ($\Delta H°$) via the equation:

$$E = 12.8 + 0.71 \times \Delta H°$$

The A-factors are calculated from the $\Delta S°$ for the reaction, together with an estimated A-factor for the reverse reaction (A_R):

$$\log A = \log A_R + \Delta S°/R$$

For radicals containing < 6 heavy atoms, the rate constants for the decomposition are expected to be in the pressure fall-off region at 1 atm pressure. k/k_∞ values were taken from the work of Baldwin *et al*. [16].

There appear to be some discrepancies in Table I and Table II of the Baldwin *et al*. [16] paper, as noted by A&L [3].

19b. Niki and coworkers [33] have obtained information on the relative rates of the reactions of the β-hydroxy alkoxy radical, $HOCH_2CH_2\dot{O}$, by generating these radicals from the photo-oxidation of C_2H_4 in air and monitoring the products by FTIR. Thus, from the yields of the products HCHO and $HOCH_2CHO$ at 760 Torr of air at 298 K they deduced that $k_2/k_1 = 5.4 \times 10^{-20}$ cm^3 $molecule^{-1}$ for the reactions:

$$HOCH_2CH_2\dot{O} \xrightarrow{(1)} HCHO + CH_2OH$$

$$HOCH_2CH_2\dot{O} + O_2 \xrightarrow{(2)} HOCH_2CHO + HO_2$$

This means that the fraction of $HOCH_2CH_2O$ reacting with O_2 is 0.22 under these conditions.

These experiments are in disagreement with the expectations based upon thermochemical estimates for these reactions. Thus, for reaction (1) we calculated $\Delta H° = 7.7$ kcal mol^{-1} and $\Delta S° = 35.7$ cal mol^{-1} K^{-1} (standard state 1 atm) from which it follows by the procedures outlined in note 19a that $E_1 = 18.3$ kcal mol^{-1} and $\log(A/s^{-1}) = 14.3$. Thus, $k_{298} = 7.6 \times 10^0$ s^{-1}. Since, however, the radical decomposition reaction is likely to be in the pressure fall-off region, at 1 atm pressure with $k/k_\infty = 0.6$ (Baldwin et al. [16], this yields $k_1 = 4.5 \times 10^0$ s^{-1} at 298 K and 1 atm pressure. For reaction (2) we estimate that $\Delta H° = -32.7$ kcal mol^{-1} leading to $k_2 = 6.2 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} (see note 15). On the basis of these thermochemical estimates it follows that fraction of $HOCH_2CH_2O$ reacting with O_2 is close to unity. There is some additional evidence from FTIR studies [34] of the photooxidations of C_3H_6 and trans-2-C_4H_8 that the β-hydroxyalkoxy radicals $CH_3CHOHCH_2\dot{O}$, $CH_3CH\dot{O}CH_2OH$ and $CH_3CH\dot{O}CHOHCH_3$ also undergo considerably more decomposition than reaction with O_2.

At present we are unable to explain the large discrepancy between the experimental data of Niki et al. [33,34] and the thermochemical calculations. We have adopted the recommendation of Atkinson and Lloyd [3] that for these β-hydroxyalkoxy radicals the decompositions are rapid relative to reaction with O_2. From the experimental value of $k_2/k_1 = 5.4 \times 10^{-20}$ cm^3 molecule^{-1} and $k_2 = 6.2 \times 10^{-15}$ cm^3 molec^{-1} s^{-1} it follows that $k_1 = 1.1 \times 10^5$ s^{-1}, and this is the rate constant which we have selected for the decompositions of the other β-hydroxyalkoxy radicals as well.

As regards the temperature coefficient of the reaction of the type

$$HOCH_2CH_2\dot{O} \rightarrow HCHO + CH_2OH$$

taking $k_{298} = 1.1 \times 10^5$ s^{-1} and estimating an A-factor of $10^{13.5}$ s^{-1} (by analogy with $n\text{-}C_3H_7 \rightarrow CH_3 + C_2H_4$), it follows that E = 11.5 kcal mol^{-1}.

20. We have adopted the recommendation of A and L [3] that for this class of reaction

$$R_2\dot{C}OH + O_2 \xrightarrow{(1)} R_2C{=}O + HO_2$$

the rate constant appears to be abnormally high; i.e., $k \sim 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, in relation to the analogous reactions of alkoxy radicals

$$R_2C\dot{O} + O_2 \xrightarrow{(2)} \text{carbonyl cpd.} + HO_2.$$

Thus we estimate $\Delta H°(1) \simeq -22$ kcal mol^{-1} and $\Delta H°(2) \simeq -35$ kcal mol^{-1} and consequently on thermochemical grounds it would be anticipated that $k_2 > k_1$. More experimental information is required on reaction (1).

21. The fractions of OH attack at the different types of C-H bonds in the molecule have been calculated from the equation of Atkinson *et al*. [35]:

$$k = 1.01 \times 10^{-12} N_1 \exp(-823/T) + 2.41 \times 10^{-12} N_2 \exp(-428/T) + 2.10 \times 10^{-12} N_3 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where N_1, N_2 and N_3 are the numbers of primary, secondary and tertiary C-H bonds in the molecule.

22. We have calculated the rate constants for alkoxy radical isomerization reactions according to the procedures described by Baldwin _et al_. [16]. On energetic grounds the reactions are most favorable when they involve 5 or 6 member ring transition states for which the A-factors have been estimated to be $10^{11.2}$ and $10^{10.9}$ s^{-1}, respectively, per H atom available for reaction. The activation energies were estimated from the activation energies for H-abstraction by alkoxy radical; i.e., (C-H) prim = 7.2, (C-H) sec = 6.0 and (C-H) tert = 4.1 kcal mol^{-1}, and adding strain energies of 0.5 kcal mol^{-1} for 6-atom ring reactions and 5.9 kcal mol^{-1} for 5-atom ring reactions. The results for the most frequently occurring combinations of mechanisms are as follows:

	k_{isom}/s^{-1}	
Number and type of (C-H)	5-Atom Ring	6-Atom Ring
1 tert (C-H)	7.3×10^3	3.4×10^7
2 sec (C-H)	5.9×10^2	2.7×10^6
3 prim (C-H)	1.2×10^2	5.7×10^5

23. The absolute rate constants for the Criegee intermediates (CH_2OO, CH_3CHOO, etc.) have not been determined, and there are few data related to their relative values for the tropospheric constituent molecules. The values chosen here are in accord with the

recommended range of values given by Herron et al. [3]. The most significant differences between these estimates and those of Atkinson and Lloyd [3] are the chosen values for the CH_2OO-NO_2, CH_2OO-H_2O, and the CH_2OO-SO_2 rate constants. Recent data of Suto et al. [38], not available to the previous authors at the time of their review, defined the choice made here. The CH_2OO-SO_2 rate constant chosen for our mechanism is an order of magnitude larger than that picked by Atkinson and Lloyd. See the more detailed discussion of the text, section III-c-ii-b and Tables II and III.

24. Using the rate data described in note 21, we calculate the fraction of the two channels to be 0.08 and 0.92 rather than 0.14 and 0.86 given by Leone and Seinfeld [1].

25. Adapting the procedures described in note 18, we estimate the fractions of the two channels of RO_2 reaction with NO to be 0.83 and 0.17 rather than 0.9 and 0.1 chosen by Leone and Seinfeld [1]. Similar differences exist in the other competitive reactions of this type.

26. The detailed reaction sequences which occur subsequent to the formation of the HO-aromatic hydrocarbon-O_2 adducts are not well established. The reactions suggested here and elsewhere in the literature are based in large part upon the analogous reactions observed in the simpler hydrocarbon systems and on the limited product analyses of the aromatic hydrocarbon oxidations which have been reported [49-53].

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C) The NCAR Master Mechanism of the Gas Phase Chemistry

Through an extrapolation of the considerations based upon the mechanism of Table I we have formulated a more complete mechanism which we have designated as our "Master Mechanism of the Gas Phase Chemistry". This complete mechanism is given in the Appendix A of the this volume of the report. Atkinson and Lloyd have reviewed well the literature related to the chemistry of oxidant and acid generation in the troposphere, and where we concur with their judgement and rate constant choices, a further discussion of these data is unnecessary. It is the major purpose of this section to discuss in more detail the reasons for our particular rate constant choices which, in a small number of cases, differ from those of Atkinson and Lloyd. Additional chemistry of the natural occurring sulfur and nitrogen compounds, included in the NCAR master mechanism but not considered by Atkinson and Lloyd (1984), is also reviewed here.

i) The Inorganic NO_x, HO_x, O_x, and SO_x Chemistry (reactions 1 through 93 of the Master Mechanism, Appendix A)

a) Hydrogen Peroxide Generation

The gas-phase reactions 15 and 16 control the generation of hydrogen peroxide, the most important reactant for the liquid-phase oxidation of bisulfite ion to sulfuric acid. Fortunately the various rate data on these reactions appear to be reliable and reasonably consistent with one another.

15) $2\ HO_2\ (+M) \dashrightarrow H_2O_2 + O_2\ (+M)$

16) $2\ HO_2 + H_2O\ (+M) \dashrightarrow H_2O_2 + H_2O + O_2\ (+M)$

The effect of water vapor on the rate constant for H_2O_2 formation can be seen in Figure 1. Note that the average second order rate constant for H_2O_2 formation shows a proportional increase with H_2O vapor concentration. The results of Sander et al. (1982) at 100 (triangles) and 700 torr (diamonds) of N_2 indicate that the water effect is independent of the total pressure of the nitrogen as well. The combined data of the many investigators shown in Figure 1 are in reasonable agreement and give the following relation for the ratio of the apparent second order rate constants for hydrogen peroxide formation in the presence of water vapor $\{k(H_2O)\}$ and the absence of H_2O vapor (k):

$$k(H_2O)/k = 0.97 \pm 0.07 + (0.07 \pm 0.01)P_{H2O}$$

where P_{H2O} is in torr. The sensitivity of the rate constant for H_2O_2 generation to the $[H_2O]$ results in a doubling of the rate constant with increase in P_{H2O} from 0 to 14 torr. We recommend that the overall rate constant for hydrogen peroxide formation which has been suggested by Kircher and Sander (1984) be used:

$$d[H_2O_2]/dt = [HO_2]^2(k_a + k_b)\{1 + 1.4 \times 10^{-21}e^{2200/T}\}[H_2O]$$

$$k_a = 2.2 \times 10^{-13}e^{620/T}\ cm^3\ molec^{-1}\ s^{-1}$$

$$k_b = 1.9 \times 10^{-33}[M]e^{980/T}\ cm^3\ molec^{-1}\ s^{-1}$$

where [M] is the concentration of air (N_2/O_2) in molecules cm^{-3}.

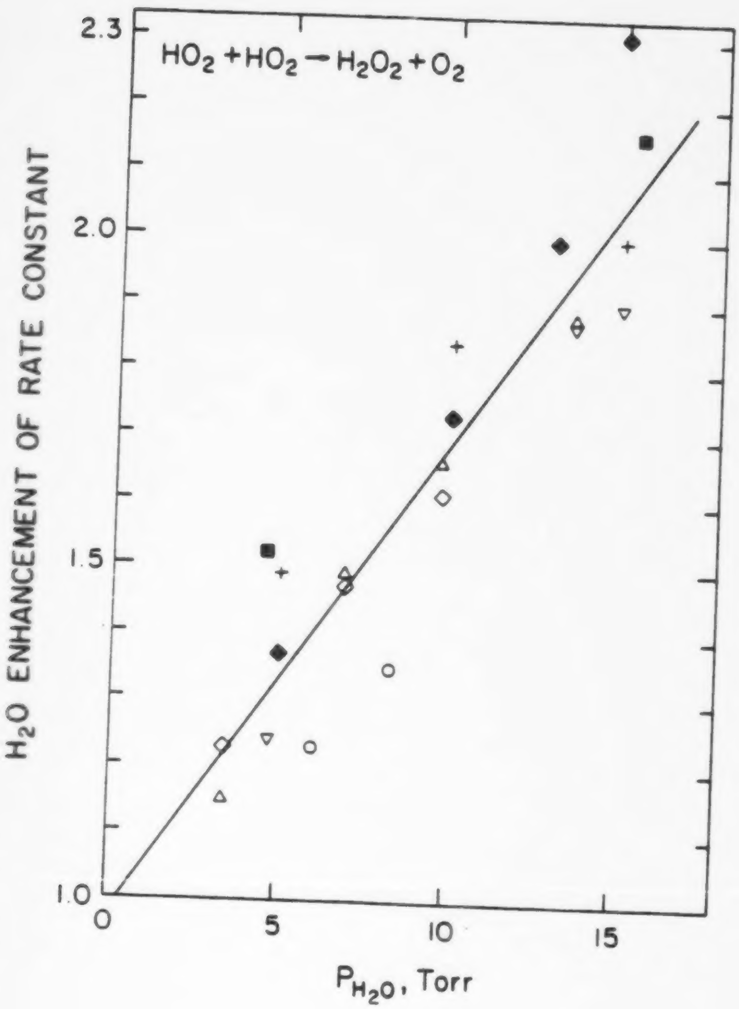


Figure 1. The water enhancement factor on the gas phase rate constant for hydrogen peroxide formation versus pressure of H_2O; data shown are from: Sander et al. (1982), 100 torr air, triangles; 700 torr air, open diamonds; DeMore (1979), filled squares; Lii et al. (1981), inverted triangles; Hamilton (1975), plus signs; Hamilton and Lii, closed diamonds; Cox and Burrows (1979), circles; after Sander et al. (1982).

b) The NO_x Chemistry

The NO_x chemistry is very important in the mechanism of acid generation within the troposphere. Particularly important for the nighttime chemistry are the reactions of the free radical NO_3. There are some relatively new features of this NO_x chemistry which we have accepted in the above mechanism and which differ somewhat from that of Atkinson and Lloyd. In particular, the reactions 30-32 have been added here in view of recent studies by Cantrell et al.(1984) and Johnston et al.(1984).

30) $NO_2 + O_3 \rightarrow NO + O_2$

31) $NO_3 + M \rightarrow NO + O_2 + M$

32) $NO_3 + HO_2 \rightarrow HONO_2 + O_2$

A reasonable explanation for the observed unusual stoichiometry of the reaction,

6) $NO_2 + O_3 \rightarrow NO_3 + O_2$,

involves the new channel 30 which presumably occurs from a fraction of the vibrationally rich NO_3 initial product of reaction 6. Evidence is strong from several experiments that the thermal decomposition of NO_3 occurs by reaction 31 at atmospheric pressures and temperatures. The lifetime of NO_3 from this process in the lower troposphere is estimated to be about 10^3 sec. The reaction between HO_2 radicals and NO_3 has been postulated to explain the observed decay rates of NO_3 in N_2O_5-CH_2O-O_2 mixtures (Cantrell et al., 1984).

The reactions of the NO_3-radical with a great variety of compounds (hydrocarbons, aldehydes, etc.) have been studied in recent years (Morris and Niki, 1974; Japar and Niki, 1975; Hoshimo et al., 1978; Bandow et al., 1980; Pitts et al., 1984; Atkinson et al., 1984; Winer et al., 1984; Cantrell et al., 1984.) In the most recent studies of Cantrell et al. (1984) the time dependence of all of the products and reactants were determined in dilute NO_2-O_3-CH_2O mixtures in N_2/O_2, and the rate constant for the reaction of NO_3 with CH_2O was estimated to be $(6.3 \pm 1.1) \times 10^{-16}$ cm^3 $molec^{-1}$ s^{-1} (298 K). Atkinson et al. (1984) recently reported this constant to be $(3.23 \pm 0.26) \times 10^{-16}$ cm^3 $molec^{-1}$ s^{-1} based upon experiments in which the N_2O_5 decay rate alone was followed; the NO_3-radical concentration was calculated using measured $[NO_2]$ and $[N_2O_5]$ and the Malko and Troe recommended value for the equilibrium constant for $N_2O_5 \Leftrightarrow NO_3 + NO_2$. However recently Tuazon et al. (1984) have redetermined this equilibrium constant and reported a value which is lower by a factor of 1/1.8 than that which the same research group had employed in their studies of the NO_3 rate constants. Tuazon et al. noted that all of the recently reported NO_3-RH rate constants from the Pitts′ group would be raised by a factor of 1.8 if they used their newly measured K_{eq} values. If we combine their equilibrium and rate constant data for the NO_3-CH_2O system, we find the desired rate constant, $k = (6.0 \pm 0.5) \times 10^{-16}$ cm^3

$molec^{-1}\ s^{-1}$, in excellent agreement with the value of Cantrell et al. In our judgment it is imperative to use the equilibrium constant which was determined with the same equipment, the same extinction coefficient calibration data, and same procedures which were employed in deriving the rate constant estimates. Thus we have raised all of the reported NO_3-radical rate constants of the Pitts' group by the factor 1.84 to derive the recommended rate constants given in the master mechanism. See Cantrell et al., 1984.

Recent direct measurements of Perner et al. (1984) support the constants for the $N_2O_5 <=> NO_3 + NO_2$ equilibrium reported by Graham and Johnston (1978), and we have employed these data in our master mechanism. Note $K_{eq} = k_{27}/k_{26}$.

c) The Gas-Phase Chemistry of Ammonia (NH_3)

Acids which are generated in the troposphere may be neutralized in part through reactions with basic compounds such as gaseous NH_3, carbonate-containing aerosols, etc. Since gaseous ammonia is a ubiquitous gas released into the troposphere from both natural and anthropogenic sources, both the gas- and the liquid-phase chemistry of ammonia must be considered in modeling acid generation in the troposphere. The ammonia chemistry shown in reactions 40-50 is based in part upon recent experimental measurements and in part on thermochemical kinetic considerations.

40) $HO + NH_3 \rightarrow H_2O + NH_2$

41) $NO_3 + NH_3 \rightarrow HONO_2 + NH_2$

42) $NH_2 + O_2\ (+M) \rightarrow NH_2O_2$

43) $NH_2O_2 + NH_2O_2 \rightarrow 2NH_2O + O_2$

44) $NH_2O_2 + NO \rightarrow NH_2O + NO_2$

45) $NH_2 + NO \rightarrow N_2 + H_2O$

46) $NH_2 + NO_2 \rightarrow N_2O + H_2O$

47) $NH_2 + O_3 \rightarrow NH_2O + O_2$

48) $NH_2O + O_2 \rightarrow HNO + HO_2$

49) $HNO + hv \rightarrow H + NO$

50) $HNO + O_2 \rightarrow HO_2 + NO$

The sources of these data are referenced in Table I. The NO_3-NH_3 reaction has been observed to occur at a significant rate in dilute N_2O_5-NH_3 mixtures in O_2/N_2 mixtures; The rate constant is now under study.

It should be noted that the upper limit set on the reaction 42 does not exclude the occurrence of 41 at the pressures of oxygen found in the troposphere. The involvement of the NH_2O_2 radical in the mechanism of NH_3 oxidation was favored by Jayanty et al., but the rate constants for the reactions related to it are highly uncertain. Those which are assigned in the Master Mechanism are based upon analogous reactants and thermochemical kinetic estimates.

d) The Gas-Phase Chemistry of Sulfur Dioxide (SO_2)

There is general agreement that the most important of the gas-phase mechanisms for SO_2 oxidation to sulfuric acid involves the HO-SO_2 reaction. We have reviewed the available kinetic data related to reaction 51, and these data are plotted in Figure 2.

51) $HO + SO_2\ (+M) \rightarrow HOSO_2\ (+M)$

Wine et al.(1984) recommend from their most recent work the function defined by the long-dashed curve of Figure 2. This function when extrapolated to the high pressure region of 1 atm and 298 K, leads to their recommended value of 8.0×10^{-13} cm^3 $molec^{-1}$ s^{-1}. It is clear from Figure 2 that the extrapolated curve of Wine et al. misses badly the many high pressure and low pressure data points which are also of seemingly high quality. In Figure 3 the same data are shown with the least squares fit of all but the first measurements of the constant made by Davis et al. and Harris and Wayne. We recommend the use of this curve for rate constants as a function of air concentration and at 298 K; it is defined by:

$$\ln(1/k_{51}) = 110.7758 + 3.19531\ln(1/[M]) + 2.9808 \times 10^{-2}\{\ln(1/[M])\}^2$$

Here [M] is the concentration of air in molecules/cm^3. Our data choices for reaction 51 which result from this evaluation, check reasonably well with that of the NASA and CODATA evaluations (see

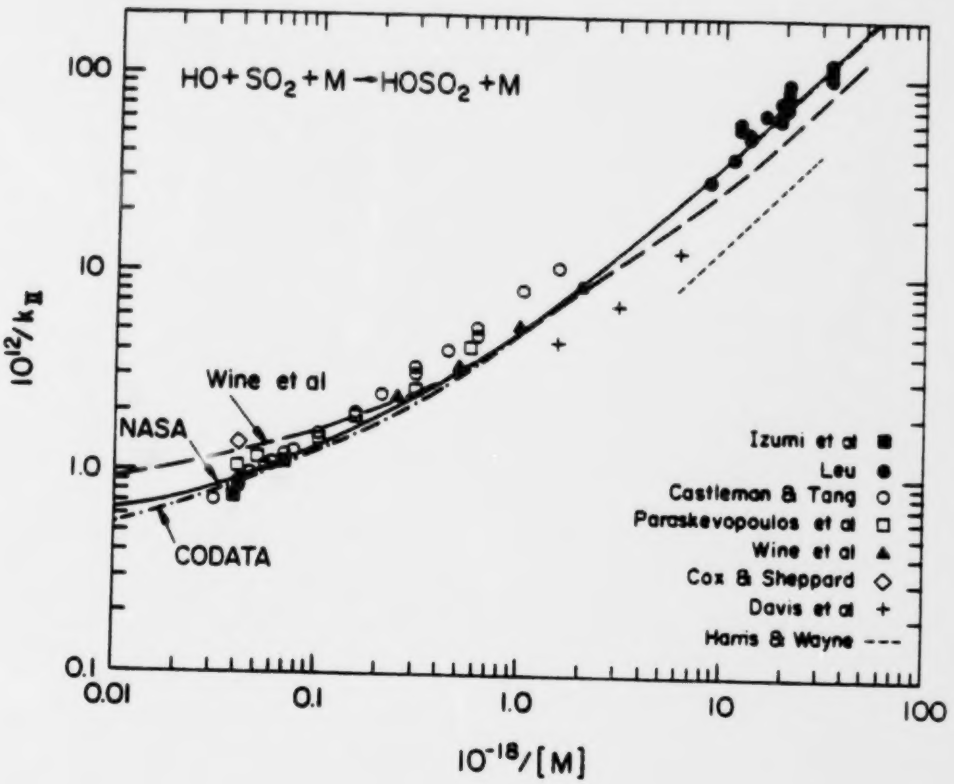


Figure 2. Plot of the reciprocal of the apparent second order rate constant (cm^3 molec^{-1} s^{-1}) for the reaction between SO_2 and HO versus the reciprocal of the concentration of air or N_2 (molec cm^{-3}) for temperatures near 25°C; literature references to the various data sources are given in the text.

Figure 3), but they are significantly larger than those recommended by Atkinson and Lloyd and Wine et al.

The temperature coefficient for the HO-SO_2 reaction has been determined by a number of workers. These data have been reviewed by the NASA and CODATA panels. This coefficient is a function of pressure. We have plotted the average of the E_{51}/R values suggested by the two panels versus the pressure in Figure 4. We recommend that the least squares fit to these data be used as the best estimate of the appropriate activation energy parameter:

$$-(E_{51}/R)\ K = 3.6896 \times 10^{-4}\ P^2 - 6.793 \times 10^{-1}\ P + 5.3374 \times 10^2$$

where P is the pressure of air in torr.

e) The Tropospheric Chemistry of Hydrogen Sulfide (H_2S)

Hydrogen sulfide represents largely a natural source of sulfur, and an account of its contribution to the SO_2 and sulfuric acid in the troposphere is important to our considerations. The detailed elementary steps involved in the chemistry of the natural sulfur-containing compounds are incompletely understood today. Although the nature of the elementary step in the HO-H_2S reaction appears to be described well by reaction 55, the subsequent reactions of the HS radical are open to question for conditions of high O_2/N_2 concentrations present in the troposphere.

55) $HO + H_2S \dashrightarrow H_2O + HS$

Recent measurements made in the NCAR laboratories show that

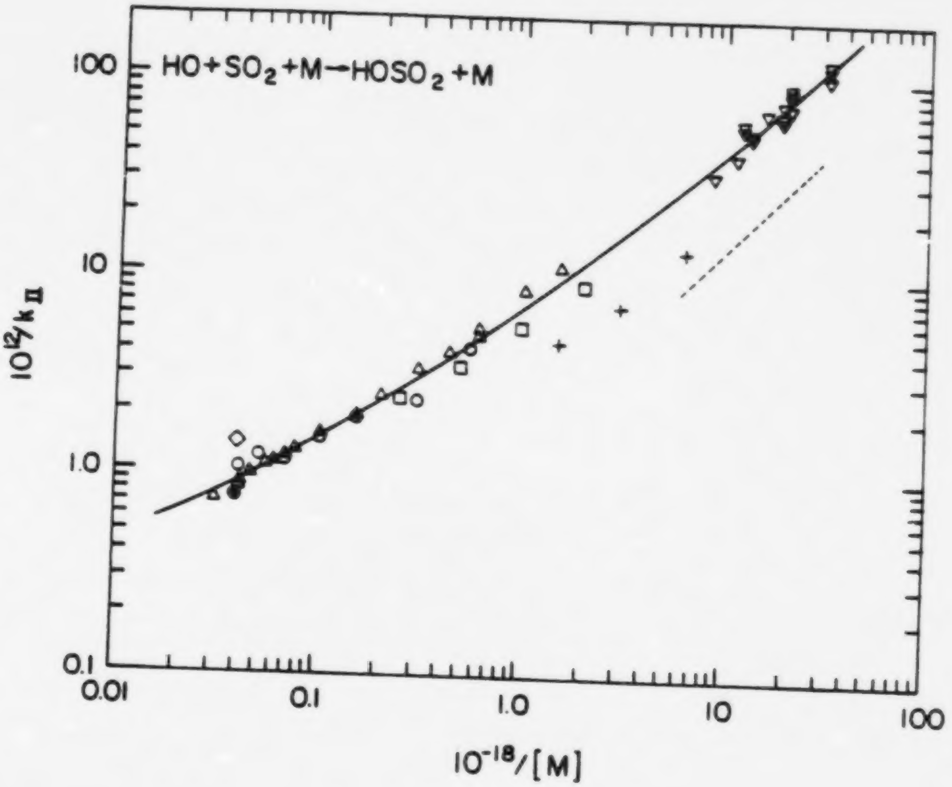


Figure. 3. Plot of the reciprocal of the apparent second order rate constant (cm^3 molec^{-1} s^{-1}) for the reaction between SO$_2$ and HO versus the reciprocal of the concentration of air (molec cm^{-1}) for temperatures near 25°C; data are from Leu (1982), inverted triangles; Castleman and Tang (1976/1977), triangles; Paraskevopoulos, et al. (1983), open circles; Wine et al. (1984), squares; Cox and Sheppard (1980), diamonds; Davis et al. (1975), plus signs; Izumi et al. (1983), filled circles; Harris and Wayne (1975), locus of data, dashed curve.

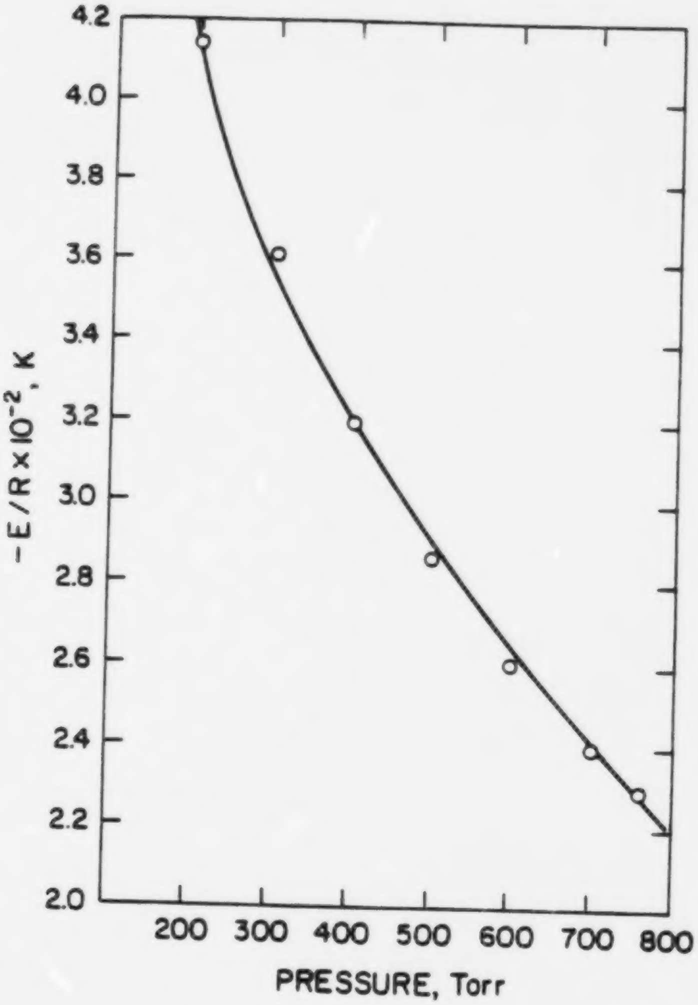


Figure 4. Plot of the activation energy function (-E/R, K) versus the presure of air (torr) for the HO-SO_2 reaction; the plotted points are the average of the values recommended by the NASA-6 and CODATA-3 reviews.

the NO_3-H_2S reaction also occurs readily, although reliable rate constant estimates have not yet been derived from the data. We have assumed in the present mechanism that the reaction 56, of near equal enthalpy change to that for the analogous NO_3-CH_2O reaction, occurs with the same rate constant.

56) $NO_3 + H_2S \text{ --> } HONO_2 + HS$

The recent studies of Friedl et al. give new rate data for the reactions of HS with O_2, O_3, NO_2 and HSO with O_3:

58) $HS + O_2 \text{ --> } HO_2 + S$

60) $HS + O_3 \text{ --> } HSO + O_2$

62) $HS + NO_2 \text{ --> } HSO + NO$

63) $HSO + O_3 \text{ --> } HS + 2\ O_2$

The removal of the HS radical by reaction with O_2 is unimportant, at least at low pressures of O_2 present in the experiments of Friedl et al., so the combined result of the occurrence of reactions 58-63 is the destruction of O_3, catalyzed by the HS free radical reactions. Since the data were obtained at low pressures evidence for the possible significance of the HS-O_2-M coupling reaction 57 at tropospheric pressures could not be obtained.

57) $HS + O_2\ (+M) \text{ --> } HSO_2\ (+M)$

Results of Cox (1975) show clearly that NO is oxidized to NO_2 in irradiated H_2S-HONO-NO-NO_2-air mixtures at 1 atm pressure. Also results of Thiemens and Schwartz (1978) show that the photolysis of dilute mixtures of H_2S in air resulted in an amount of SO_2 roughly equal to the H_2S lost. Both of these results show clearly that at pressures of air available in the lower troposphere, reaction 57 must occur, and it is likely that this is followed largely by reaction 59 to form SO_2. Thus we conclude from the very limited evidence at hand that reactions 55, 56, 57, and 59 may describe the important tropospheric reactions of H_2S.

59) $HSO_2 + O_2 \rightarrow HO_2 + SO_2$

f) The Chemistry of Dimethyl Sulfide (CH_3SCH_3)

The detailed chemistry of the dimethylsulfide is also poorly defined today. Several studies have been made of the photooxidation of CH_3SCH_3 in air and in NO_x- or HONO-NO_x-containing dilute mixtures in air (Bentley et al., 1972; Cox, 1975; Hatakeyama et al., 1982; Grosjean and Lewis, 1982; Niki et al., 1982; Niki et al., 1983; Grosjean, 1984), and the elementary rate constants for the HO-CH_3SCH_3 and NO_3-CH_3SCH_3 have been determined by Atkinson et al. (1984); Wine et al. (1981); Cox and Sheppard (1980); Atkinson et al. (1978); Kurylo (1978).

Presumably the reactions of the HO and NO_3 radicals are the major sinks for CH_3SCH_3 in the troposphere. Although rate constants for these reactions have been determined within a factor of 2.5, the mechanism of the initial attack and the subsequent reactions of the initial transient products are still open to question. It has been observed by Hatakeyama et al. (1982) and Niki et al. (1982, 1983) that when dimethylsulfide reacts with HO-radicals about 20% of the sulfur in CH_3SCH_3 ends up ultimately as SO_2, and a large share of the balance of the sulfur appears ultimately as methane sulfonic acid, CH_3SO_3H. Interesting new compounds of sulfur and nitrogen, CH_3SNO and CH_3SNO_2, have been observed as major products also in laboratory experiments involving CH_3S-radicals at relatively high NO and NO_2 concentrations. It is not clear whether these compounds will form significantly under the more typical conditions encountered in the troposphere (low [NO] and [NO_2]). It is not possible to prove unambiguously the detailed mechanism of the reactions which lead to these products from the data available today. There are two different initial reaction pathways which have been considered for the HO-radical reaction: the removal of an H-atom in 64a and the addition of the HO-radical to the sulfur atom in 64b:

64a) $HO + CH_3SCH_3 \dashrightarrow H_2O + CH_3SCH_2$

64b) $HO + CH_3SCH_3 \dashrightarrow CH_3S(OH)CH_3$

The published data related to dimethylsulfide oxidation in air show clearly that some type of peroxy radicals capable of oxidizing NO to NO_2 are involved in the reactions which follow HO-radical attack on CH_3SCH_3. In theory subsequent reactions of the products of either 64a or 64b would fulfill this requirement and also lead to the major sulfur-containing products, SO_2 and CH_3SO_3H. Both the CH_3SCH_2 and $CH_3S(OH)CH_3$ radicals will likely react quickly with O_2 to generate peroxy radicals. However in the case of the $CH_3S(OH)CH_3$ radicals, the alternative pathway

(88) exists which can lead to dimethylsulfoxide (CH_3SOCH_3); this is analogous to the well-studied reaction 59 of the $HOSO_2$ radical involved in the oxidation of SO_2 by HO-free radicals.

a) $CH_3SCH_2 + O_2 \dashrightarrow CH_3SCH_2O_2$

87) $CH_3S(OH)CH_3 + O_2 \dashrightarrow CH_3S(OH)(O_2)CH_3$

88) $CH_3S(OH)CH_3 + O_2 \dashrightarrow CH_3SOCH_3 + HO_2$

Through the reactions of the peroxy radicals formed in (a) and (87) with NO or other peroxy radicals,other radical species are expected to form:

67) $CH_3SCH_2O_2 + NO \dashrightarrow CH_3SCH_2O + NO_2$

90) $CH_3S(OH)(O_2)CH_3 + NO \dashrightarrow CH_3S(OH)(O)CH_3 + NO_2$

It is possible that the decomposition and rearrangement of the initial product radical of 64b could generate the CH_3SO_3H:

89) $CH_3S(OH)(O_2)CH_3\ (+O_2) \dashrightarrow CH_3S(OH)O_2) + CH_3O_2$

$CH_3S(OH)(O_2) \dashrightarrow CH_3SO_3H$

The $CH_3S(OH)(O)CH_3$ product of 90 could lead to SO_2:

91) $CH_3S(OH)(O)CH_3\ (+O_2) \dashrightarrow CH_3SO(OH) + CH_3O_2$

92) $CH_3SO(OH)\ (+O_2) \dashrightarrow CH_3O_2 + SO(OH)$

93) $SO(OH) + O_2 \dashrightarrow SO_2 + HO_2$

However if this mechanism alone were operative as a source of CH_3SO_3H and SO_2 then one expects that the fraction of the initial CH_3SCH_3 which would lead to SO_2 would be a sensitive function of the [NO]. This has not been reported, although it has not been tested for explicitly to our knowledge.

The alternative mechanism of 64a which leads to $CH_3SCH_2O_2$

and subsequently CH_3SCH_2O radical generation, may in theory also generate the SO_2 and CH_3SO_3H products by way of reactions 70-86 in the master mechanism, where CH_3S, CH_3SO, CH_3SO_2, and CH_3SO_3 radicals participate. This reaction pathway is favored by Niki et al. (1983). However in view of the relatively low enthalpy changes involved in the decomposition reactions of the CH_3SO_2 and CH_3SO_3 radicals,

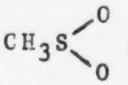
81) CH_3SO_2 (+M) --> $CH_3 + SO_2$; $\Delta H \cong 17$ kcal mole^{-1}

83) CH_3SO_3 (+M) --> $CH_3 + SO_3$; $\Delta H \cong 22$ kcal mole^{-1},

the other competitive reactions of these radicals which are necessary to lead to CH_3SO_3H have to be very rapid if this mechanism is to be a viable alternative. The exothermicity of the CH_3SO_3 and NO_3 abstraction reactions from a given organic molecule are roughly the same, so as a first approximation we have assumed rate constants for the CH_3SO_3 reactions with the organic molecules to be equal to those measured for NO_3. With this assumption the decomposition of the CH_3SO_3 and CH_3SO_2 radicals in 81 and 83 will dominate over H-atom abstraction reactions of these radicals with the aldehydes and alkanes which are present at levels typical of tropospheric air masses.

There is some evidence which suggests that the H-atom abstraction pathway of the HO-CH_3SCH_3 reaction occurs a significant fraction of the time. In the work of Niki et al. (1983), the fractions of the CH_3S radicals (generated from the photolysis of

CH_3SNO) which react to form SO_2 and other products (including CH_3SO_3H), are about the same as those observed from experiments involving the CH_3SCH_3 oxidation initiated by HO-radicals. This suggests strongly that CH_3S is involved in the mechanism, since the H-atom abstraction route appears to be the only pathway which could generate the CH_3S radical.

In the considerations of Niki et al., two different structural forms,  $CH_3S\genfrac{}{}{0pt}{}{\diagup O}{\diagdown O}$ and CH_3SO_2 (bonding in this species was not defined), are suggested to exist. They propose that the CH_3SO_2 species would lead to SO_2 and CH_3-radicals, and the other isomer formed, ". . . would eventually lead to CH_3SO_3H, analogously to the formation of H_2SO_4 in the HO-initiated oxidation of SO_2." The analogy is not clear to these authors, and we remain unconvinced of the singular importance of the reaction channel 64a in the HO-radical reaction with CH_3SCH_3.

In view of the uncertainties associated with the detailed mechanism of CH_3SCH_3 oxidation in the troposphere, it is recommended that for the present the reaction sequence initiated by 64 and 65 be represented by the following overall reactions:

$$HO + CH_3SCH_3 \dashrightarrow H_2O + 0.8\ CH_3SO_3H + 0.2\ SO_2 + 1.2\ CH_3O_2$$

$$NO_3 + CH_3SCH_3 \dashrightarrow HONO_2 + 0.8\ CH_3SO_3H + 0.2\ SO_2 + 1.2\ CH_3O_2$$

The net result of the generation of 1.2 CH_3O_2 radicals per dimethylsulfide molecule oxidized would be qualitatively consistent with the observed 2.0 molecules of NO which is oxidized to NO_2 per CH_3SCH_3 reacted. This follows from the fact that for the relative high [NO] employed by Niki et al., each CH_3O_2 will oxidize an NO molecule and ultimately provide an additional HO_2 radical which will then oxidize a second NO molecule.

$CH_3O_2 + NO \rightarrow CH_3O + NO_2$

$CH_3O + O_2 \rightarrow CH_2O + HO_2$

$HO_2 + NO \rightarrow HO + NO_2$

Obviously as our knowledge of these systems improves a more realistic, detailed mechanism should be adopted.

ii) The Hydrocarbon Chemistry (reactions 94 through 409 of the Master Mechanism, Appendix A)

a) The Alkanes (reactions 94 through 172 of the Master Mechanism, Appendix A)

The master mechanism treats the reactions of several of the simple alkanes which are of interest in both the clean and the polluted troposphere; rather explicit, detailed chemistry is considered for methane, ethane, propane, n-butane, isobutane, and 2,3-dimethylbutane; a more generalized reaction sequence is given for the higher alkanes: pentanes, hexanes, heptanes, and octanes.

The tropospheric reactions of the alkanes are initiated in large part by the H-atom abstraction reactions of the HO-free radical:

$HO + RH \rightarrow H_2O + R$

$R + O_2 \ (+M) \rightarrow RO_2$

For the more reactive alkanes some reaction also occurs with the NO_3-radical and the $O(^3P)$-atom. For the conditions normally encountered in the troposphere, the $O(^3P)$-atom reactions with the alkanes are negligible, since the capture of the O-atom by oxygen ($O(^3P) + O_2 + M \rightarrow O_3 + M$) is very highly favored. For smog chamber simultions which are sometimes carried out at very high reactant concentrations, the reactions such as, $O(^3P) + RH \rightarrow HO + R$, may compete with ozone formation. However these reactions of the $O(^3P)$-atom can be neglected for tropospheric conditions. The rate constants which we have chosen for the HO-RH reactions are those recommended by Atkinson and Lloyd, 1984.

In the polluted troposphere the subsequent reactions of the alkylperoxy radicals formed following HO-radical attack on the alkanes involve largely a competition between NO oxidation and nitrate formation:

$$RO_2 + NO \rightarrow RO + NO_2$$

$$RO_2 + NO \rightarrow RONO_2$$

The pattern of distribution of these two reaction modes depends on the structure of the R species, the temperature and the pressure. The procedures we have employed to select these rate constants, based upon the work of Atkinson and Lloyd, are set forth in the note 18 following Table I. In general the greater the number of carbon atoms in the alkylperoxy radical the larger the fraction of the reaction which proceeds to form the nitrate

($RONO_2$). In the fairly clean troposphere, RO_2 radicals encounter a smaller number of NO molecules and radical-radical encounters become more common. We will discuss this type of reaction in a subsequent section.

The alkoxy radicals (RO) may react with oxygen, decompose, or rearrange with relative rates which vary with structure of the radical. They may also react with NO, NO_2, and other impurity gases in the atmosphere, although these reactions are commonly unimportant for most tropospheric conditions. For the smaller radicals (3 or less carbon atoms) the major reaction is with molecular oxygen. For example with the isopropoxy radical the following reaction channels exist:

a) $CH_3CHOCH_3 + O_2 \rightarrow CH_3COCH_3 + HO_2$

b) $CH_3CHOCH_3 \rightarrow CH_3CHO + CH_3$

c) $CH_3CHOCH_3 + NO \rightarrow CH_3CH(ONO)CH_3$

d) $CH_3CHOCH_3 + NO_2 \rightarrow CH_3CH(ONO_2)CH_3$

For concentrations of NO and NO_2 both at about 5 ppb, typical of tropospheric conditions encountered over the eastern United States, the relative rates of the four reactions shown would be: $R_a : R_b : R_c : R_d :: 1.00 : 4 \times 10^{-5} : 2 \times 10^{-5} : 3 \times 10^{-5}$. For the simple primary (RCH_2O) and secondary (R_2CHO) alkoxy radicals, the dominant reactions are those with oxygen that lead to HO_2-radicals and aldehydes or ketones.

The higher molecular weight, secondary alkyl peroxy radicals show a somewhat greater fraction of decomposition than the simple primary and secondary peroxy radicals, although reaction with oxygen is still favored strongly. Using the theoretical methods outlined in note 19 of Table I, we calculate that with the sec-butyl peroxy radical, 2% of the reaction occurs by decomposition in (a) while 98% involves reaction with oxygen in pathway (b):

a) $CH_3CHOCH_2CH_3$ --> CH_3CHO + CH_2CH_3

b) $CH_3CHOCH_2CH_3$ + O_2 --> HO_2 + $CH_3COCH_2CH_3$

The tertiary alkoxy radicals do not react with oxygen to form carbonyl species in a fashion analogous to the primary and secondary alkoxy radicals, but their dominant fate is the decomposition reaction. Thus the major pathway for the tert-butoxy free radical is the following:

$(CH_3)_3CO$ --> CH_3COCH_3 + CH_3

For the alkoxy radicals which have a chain of at least four carbon atoms attached to the O-atom, theory suggests that an internal isomerization reaction comes into play (Carter et al., 1976; Baldwin, et al., 1977). For example, consider the relative rates of the alternative reactions of the n-butoxy radical:

a) $CH_3CH_2CH_2CH_2O$ + O_2 --> HO_2 + $CH_3CH_2CH_2CHO$

b) $CH_3CH_2CH_2CH_2O$ --> $CH_2CH_2CH_2CH_2OH$

c) $CH_3CH_2CH_2CH_2O$ --> $CH_3CH_2CH_2$ + CH_2O

d) $CH_3CH_2CH_2CH_2O$ + NO --> $CH_3CH_2CH_2CH_2ONO$

e) $CH_3CH_2CH_2CH_2O$ + NO_2 --> $CH_3CH_2CH_2CH_2ONO_2$

For a tropospheric air mass with 5 ppb of NO and NO_2, the relative rates of the above reactions are in theory (See note 19a of Table I.): $R_a : R_b : R_c : R_d : R_e :: 4 \times 10^{-2} : 1.00 : 8 \times 10^{-7} : 3 \times 10^{-6} : 9 \times 10^{-6}$. Thus theory suggests that the internal rearrangement (self-abstraction) reaction dominates for this type of radical.

The generalized chemistry for the reactions of the higher alkanes has been designed to mimic that for the average of the appropriate straight chain alkane. The methods which we have used to estimate the rate constants for each of the reaction modes for the alkoxy radicals have been outlined in the notes 14, 19a, and 22.

b. Chemistry of the Alkenes (reactions 173 through 239 in the Master Mechanism, Appendix A)

The reaction mechanism for the alkenes which we have adopted is basically that recommended by Atkinson and Lloyd. There are a few differences in the rate constant choices which can be identified in the comparison of the data in Table I and the notes associated with it. In our master mechanism we consider the specific reactions of several of the simple alkenes: ethylene, propylene, trans-2-butene, and isobutene. The major differences between the mechanisms of reaction of the alkenes and the alkanes is the dominance of the HO-radical (and NO_3-radical) addition to the carbon-carbon double bond and the reactions with ozone, both of which are peculiar to the alkenes. For example the major reaction pathways for the HO-radical with ethylene in the troposphere are the following:

173) $CH_2=CH_2 + HO \dashrightarrow (HOCH_2CH_2) + O_2 \dashrightarrow HOCH_2CH_2O_2$

175) $HOCH_2CH_2O_2 + NO \dashrightarrow HOCH_2CH_2O + NO_2$

178) $HOCH_2CH_2O \dashrightarrow (HOCH_2 + CH_2O) + O_2 \dashrightarrow 2\ CH_2O + HO_2$

179) $HOCH_2CH_2O + O_2 \dashrightarrow HO_2 + HOCH_2CHO$

Note that in the case of the beta-hydroxy-alkoxy radicals (e.g., $HOCH_2CH_2O$) which are formed in these alkene systems, the fraction of the radicals which undergo decomposition is greater than that which reacts with oxygen. Thus in the above case of ethylyene, about 80% of the reaction proceeds by 178 and the 20% by 179. This is in striking contrast to the behavior of the usual alkoxy radicals described previously. See also the discussion in note 19b of Table I.

Unique to the alkene chemistry is the involvement of the so-called "Criegee intermediates" which are generated through the reaction of the alkenes with ozone. These species are of special interest here in that they oxidize SO_2 to SO_3 and sulfuric acid. However the absolute rate constants for the reactions of the Criegee intermediates (CH_2OO, CH_3CHOO, etc.) are very uncertain. No direct experimental estimates of these constants have been possible to date. Some experimental, relative rate constants for the CH_2O_2 species have been determined for SO_2, CH_2O, CO, C_2H_4, O_2, NO_2 and H_2O. Also some theoretical considerations have defined some probable limits on the absolute rate constants.

Table II compares the available experimental and theoretical estimates of these rate constants. Our estimates suggested in this work are summarized in Table III.

The enthalpy change of the reaction, $CH_2OO + NO \rightarrow CH_2O + NO_2$, (about -12 kcal/mole), is somewhat less negative (exothermic) than that for the analogous reaction, $CH_3O_2 + NO \rightarrow CH_3O + NO_2$ (about -16 kcal/mole), and the k may be somewhat less for the CH_2OO-NO reaction. In accord with the suggestion of Atkinson and Lloyd, we accept their estimate (7×10^{-12} cm^3 $molec^{-1}$ s^{-1}) for this reaction. The rate constant for the CH_2OO-SO_2 reaction has been estimated by Atkinson and Lloyd to be about 1/100th that of the CH_2OO-NO reaction, although the enthalpy change for the former reaction is about 6 kcal/mole more exothermic. We have arbitrarily set the rate constant for the CH_2OO-SO_2 reaction equal to that for the CH_2OO-NO reaction; this probably represents a maximum value for the rate constant, and simulation results obtained using these estimates must be considered to give a maximum contribution to the oxidation of SO_2 by the Criegee intermediates. Certainly if the contribution of the Criegee intermediates is unimportant for the rate contant choices made here, then we can be confident that the formation of acid by this route is unimportant in the troposphere. Recent data show that the rate constant for the CH_2OO-NO_2 reaction is about 0.014-times that for the CH_2OO-SO_2 reaction, and we have accepted this estimate. This is considerably different than the value for the CH_2OO-NO_2 reaction by Atkinson and Lloyd; they suggest a value which is a factor of ten greater than that of the CH_2OO-SO_2 reaction. The recent data of Suto et al. (Table II) on the relative rate constants for the CH_2OO-SO_2 and CH_2OO-H_2O reactions, derived from light scattering measurements from the product H_2SO_4 aerosol, are in qualitative accord with that derived from direct product rate data for the CH_3CHOO reactions. Since the latter data are more direct, we have chosen to use these data. It can be seen by comparing the data of Tables II and III that the rate constant set chosen is consistent with the theoretical range of values suggested by Herron et al. However it must be emphasized that the present estimates are subject to a large uncertainty.

Table II. Published Rate Constant Estimates for the Criegee Intermediates

Reactants	Relative k (expt.)		k, cm^3 $molec^{-1}$ s^{-1} (theory)	
	Ref.(a)	Ref.(b)	Ref.(c) (estimated range)	Ref.(d)
$CH_2OO + NO$	---	---	---	7×10^{-12}
$CH_2OO + NO_2$	---	1.4×10^{-2}	1×10^{-17} to 7×10^{-14}	7×10^{-13}
$CH_2OO + H_2O$	6.0×10^{-5}	2.3×10^{-4}	2×10^{-19} to 1×10^{-15}	4×10^{-18}
$CH_2OO + SO_2$	1.0	1.0	3×10^{-15} to 7×10^{-11}	7×10^{-14}
$CH_2OO + CH_2O$	2.5×10^{-1}	---	2×10^{-16} to 8×10^{-13}	2×10^{-14}
$CH_2OO + CO$	1.8×10^{-3}	---	---	---
$CH_2OO + O_2$	---	---	$<8 \times 10^{-22}$	---

(a) F. Su, J. G. Calvert, and J. H. Shaw, J. Phys. Chem., 84 239 (1980); the reaction with H_2O was estimated by J. G. Calvert, F. Su, J. W. Bottenheim, and O. P. Strausz, Atm. Environ., 12, 197 (1978) from the data of R. A. Cox and S. A. Penkett, J. Chem. Soc., Faraday Trans. I, 68, 1735 (1972).

(b) M. Suto, E. R. Manzanares, and L. C. Lee, Detection of Sulfuric Acid Aeorosols by Ultraviolet Scattering, preprint of paper provided to the authors; this and work related to the NO_2 reaction was presented at the XVI Informal Photochemistry Conference, Harvard University, Sept., 1984.

(c) J. T. Herron, R. I. Martinez, and R. E. Huie, Int. J. Chem. Kinet., 14, 201 (1982); the data related to the O_2 reaction were calculated from the results of H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett., 46, 327 (1977).

(d) R. Atkinson and A. C. Lloyd, Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog, J. Phys. Chem. Ref. Data, 13, 315 (1984); a preprint of this valuable paper was given to the authors in advance of publication.

Table III. Rate Constant Estimates for the Reactions of the Criegee Intermediates Which Have Been Chosen for This Work[a]

Reactants	k, $cm^3\ molec^{-1}\ s^{-1}$
$CH_2OO + NO$	7×10^{-12}
$CH_2OO + NO_2$	1.0×10^{-13}
$CH_2OO + H_2O$	4×10^{-16}
$CH_2OO + SO_2$	7×10^{-12}
$CH_2OO + CH_2O$	2×10^{-12}
$CH_2OO + CO$	1.3×10^{-14}

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[a] These rate constants were chosen for the analogous reactions of all of the Criegee intermediates considered in this work (e.g., CH_2OO, CH_3CHOO, C_2H_5CHOO, etc.).

c. The Chemistry of Aromatic Hydrocarbons (reactions 240 through 325, Master Mechanism, Appendix A)

We have accepted with some minor changes most of the rate constants and, with some expansion, the reaction mechanism for the aromatic hydrocarbon species as outlined by Atkinson and Lloyd and Leone and Seinfeld. We have included the reactions of the common aromatic hydrocarbons, benzene, toluene, and m-xylene. Where differences exist between our estimates and those of the previous workers is evident in the comparison of rate constant data in Table I. It should be noted that the detailed mechanism of the tropospheric oxidation of the aromatic compounds remains highly speculative.

d. The Chemistry of the Terpenes--The Natural Hydrocarbons (reactions 326 through 409, Master Mechanism, Appendix A)

In tropospheric air masses which are relatively free from reactive, anthropogenic hydrocarbons, the natural hydrocarbons (terpenes) can in theory have a significant influence on the chemistry of ozone formation, the HO-radical concentration, and the rates of acid generation. Thus we have included in the master mechanism two representative natural hydrocarbons: isoprene and alpha-pinene. The reaction mechanisms and rate constant choices made here are based largely on the work of Lloyd et al. (1983) and Killus and Whitten (1984) with some expansion of the mechanism to include the further degradation of the products.

iii. The Chemistry of the Simple Alcohols

The HO-radical attack on only two of the simplest alcohols (methyl and ethyl alcohols) has been included in the mechanism; reactions 410 and 411 of the master mechanism. These rate data are based upon the recommendations of Atkinson and Lloyd.

iv. Additional Aldehyde and Ketone Chemistry (reactions 412 through 532, Master Mechanism, Appendix A)

All of the primary photochemical processes of the many different aldehydes and ketones which are generated in the reactions of the hydrocarbons in the master mechanism are included in this section of the reaction mechanism. There are some new suggested pathways included among these reactions which should be described here. In addition to the two major primary processes in the photolysis of formaldehyde, reactions 412 and 413, the reaction 414 is also included.

412) $CH_2O + hv \text{ --> } H_2 + CO$

413) $CH_2O + hv \text{ --> } H + HCO \ (+ O_2) \text{ --> } 2\ HO_2 + CO$

414) $CH_2O + hv \text{ --> } HCOH \ (+ O_2) \text{ --> } HC(OH)O_2$

The experimental basis for the reaction 414 was derived in matrix studies of formaldehyde photolysis by Lee and his coworkers (1978,1979,1982). Theoretical studies support the view that the primary process 414 could occur for excitation within the first absorption band of CH_2O (Frisch et al., 1981; Adams et al., 1981). Recently Martinez (1984) has suggested that perhaps the reaction 414 could be invoked to rationalize some of the unusual results obtained in photooxidation studies of formaldehyde. It is unlikely that process 414 is important for CH_2O photolysis at the wavelengths longer than 3000 A since the quantum yield of CO, expected to be the sum of the primary quantum yields of processes 412 and 413, is unity within the experimental error (Horowitz and Calvert, 1978; Moortgat and Warneck, 1979; Moortgat, et al. 1983). However at wavelengths shorter than 3000 A the quantum yield of CO falls significantly for reasons which have not been elucidated. It is possible, if not probable, that the reaction mode 414 is responsible for this, but further experimental studies must be made to evaluate this hypothesis. Note that a hydroxy-substituted Criegee intermediate is the net product of such a reaction, and reaction 414 could provide a new pathway for the generation of formic acid within the troposphere. The radical formed in 414 will not give CO on reaction with O_2 but the $HC(OH)O_2$ radical is expected as the initial product of the reaction, and formic acid (HCO_2H), peroxyformic acid ($HCOO_2H$), CO_2, and/or other possible compounds should result as the ultimate products.

The glyoxal photolysis reaction 419 is similar to that described for the formaldehyde reaction 414.

418a) $(HCO)_2 + hv \dashrightarrow 2\ CO + H_2$

418b) $(HCO)_2 + hv \dashrightarrow CH_2O + CO$

419) $(HCO)_2$ + hv --> CO + HCOH (+O_2) --> HC(OH)O_2 + CO

Our reaction 418 in the master mechanism is a condensation of the two reactions 418a and 418b using the product quantum yield data of Calvert and Layne derived from the 3130 A photolysis. Evidence for the occurrence of 419 comes from the work of Hepburn et al. who carried out molecular beam experiments and the detection of the products of the 4398 A photolysis of glyoxal under collision-free conditions. Since the process 419 can occur in theory at much long wavelengths that the analogous CH_2O reaction 414, this is an especially attractive possible source of organic acid in the troposphere. Further tests of the extent, if any, that reaction 419 occurs in the photolysis of glyoxal under tropospheric conditions must be made before a definitive conclusion is possible.

Studies of the photolyses of the higher molecular weight aldehydes and ketones have shown that several types of molecular fragmentation or rearrangement can occur (Calvert and Pitts, 1966). The simple aldehydes (RCHO) show both a free radical rupture forming formyl radicals (HCO) and alkyl radicals (R), process (I), and a molecular rearrangement to form directly carbon monoxide and a hydrocarbon, process (II):

I) RCHO + hv --> R + HCO

II) RCHO + hv --> RH + CO

Process (II) is peculiar to aldehydes and is absent in ketones.

However the ketones show a reaction mode III, similar to process I for the aldehydes:

III) RCOR′ + hv --> RCO + R′

When the R-group has a chain of 3 or more carbon atoms in length and hydrogen atoms are present in the gamma position with respect to the carbonyl group, then in addition to the primary processes I, II, and III, another type of primary process is observed to occur in both ketones and aldehydes. For the general case this reaction may be written as follows:

(IV) $HR_2CCR_2CR_2COR'$ + hv --> $CR_2=CR_2$ + $CR_2=CR'OH$

Here the $CR_2=CR_2$ molecule is an alkene, and the $CR_2=CR'OH$ molecule is an enol-form of the aldehyde or ketone of structure, HCR_2COR'. The R and R′ represent a hydrogen atom or any alkyl group such as CH_3, C_2H_5, etc. In the aldehydes R′ is always an H-atom. Studies of a large variety of ketones and aldehydes of the general form, $CH_3CH_2CH_2COR$, have been made, and relationships between the structure of these compounds and the primary quantum efficiency of the various processes has been derived (e.g., Nicol and Calvert, 1967). Process III has been found to occur in all of the molecules studied, and the primary quantum efficiencies are reasonably large, and sensitive to the structure of the R-groups in the molecule. The enol-form of the carbonyl has been shown experimentally to be a primary product in these systems, and its decay to the keto-form of the carbonyl compound is very slow in the gas phase (McMillan et al., 1964), and the evidence suggest that isomerization is probably unimportant unless the enol-compound is absorbed into highly acidic aerosol, cloud-water or ground-water solutions or onto certain solid surfaces. Process IV then provides a unique source of a reactive hydroxy-substituted alkene which in theory will react readily with both HO-radicals and with ozone in the fashion of the alkenes. However in this case we expect the products of the reactions with O_3 to include the organic acids (formic acid, acetic acid, peroxyformic acid, peroxyacetic acid, etc.); see reactions 749 through 766 of the master mechanism in Appendix A.

The J value which describe the rate of a given primary photochemical process is proportional to the integral (over the entire effective wavelength region) of the product of the wavelength dependent functions which describe the solar irradiance, the primary quantum yield of the given process, and the extinction coefficient of the compound of interest. Although there are now reasonably accurate methods of estimating the solar irradiance for the variety of atmospheric conditions, the different latitudes, times of day, and day of the year, and the absorption spectra of most compounds are well known or can be measured readily, the extrapolation of very limited experimental data related to the quantum yields of the primary processes to the hundred or so of the photochemically active species which appear in the master mechanism must entail a high degree of speculation and uncertainty. Only three of the many important carbonyl species have been studied under conditions which allow a reasonably accurate assessment of the photochemical rates for tropospheric conditions (air at atmospheric pressures). Useful quantitative data for formaldehyde (Horowitz and Calvert, 1978; Moortgat and Warneck, 1979; Moortgat et al., 1983), acetaldehyde (Horowitz and Calvert, 1982; Meyrahn et al., 1982), and acetone (Gardner et al., 1984) have been obtained, but the necessary photochemical information, including the wavelength, temperature, and air pressure dependence of the primary quantum yields are not now available for the many other carbonyl species which we identify as important in the tropospheric chemistry. Some relative photolyis rate data have been reported for glyoxal, methylglyoxal, and biacetyl by Plum et al. (1983), pyruvic acid by Grosjean (1983), and cis- and trans-3-hexene-2,5-dione by Tuazon et al. (1984) which are of limited use. These experiments were carried out in smog chambers for which it is necessary to correct for impurity release from the walls (CH_2O, NO_x, HONO, etc.) which contribute to an ill-defined, free radical source. This adds to the total induced decomposition of the species under study to complicate the interpretation, and correction of the observed rates is necessary to derive the unknown photochemical decay rates. Furthermore no information is obtained about the wavelength or pressure dependence of the photochemical processes in the chamber experiments, since a continuum of radiation of ill-defined wavelength distribution must be employed here. The assignment of photolyis rates for the various species must take into account the very limited accurate data available, but reasonable extrapolations of these data to the many other compounds as yet unstudied, is an important and necessarily complicated task which has not yet been accomplished satisfactorily by us or any other group of which we are aware. We plan further work to arrive at reasonable estimates of these critical data, but the need for more quantitative experimental work related to this problem is evident.

The reactions of the aldehydes with the HO- and NO_3-radicals are summarized in reactions 499-529 of this section as well.

v. Additional Reactions of the Alkoxy, Alkylperoxy, and Acylperoxy Radicals and Other Products of the Aldehyde Reactions.

The radical termination reactions which involve the various organic peroxy radicals and HO_2 should be included in any model to be applied to the troposphere characteristic of most nonurban areas of the United States. It is recognized that as many radical chains which are initiated in the atmosphere by the photolysis of ozone (through $O(^1D)$ and HO-radical generation), formaldehyde, acetaldehyde, etc. (HO_2, RO_2 radical generation), must be terminated at rates which are equal to those of chain initiation. If these reactions are not included in a simulation scheme, then all the RO_2 species are arbitrarily forced to find and react with NO (or NO and NO_2 in the case of the peroxyacyl radicals). When the NO is depleted, the radical concentration builds unrealistically, since there is no available pathway for reaction. With our present interest in mechanisms of acid development, it is especially important to include in simulation mechanisms the RO_2 reactions with HO_2, as the products of these reactions, the organic hydroperoxides and peroxyacids, are potential oxidants for HSO_3^- ion in aqueous cloud water which lead to the generation of sulfuric acid.

In our master mechanism we have included many of these termination reactions (reactions 533 through 634, master mechanism, Appendix A) . At present only three of the many possible RO_2-RO_2 reactions have been included, those involving CH_3O_2-CH_3O_2, $C_2H_5O_2$-CH_3O_2, and $C_2H_5O_2$-$C_2H_5O_2$. Computer simulations with the complex reactions mechanism should be made to determine the major RO_2 species in mixtures typical of commonly encountered tropospheric air masses so that the various possible RO_2-RO_2 reactions involving the major RO_2 species can be included. It is of course economically impossible to include all the possible RO_2-RO_2 reactions combinations involving the 100 different RO_2 species. We would have to include over 5000 separate reactions to do this, a choice which would be unrealistic in development of a usable chemical module. The dominance of the HO_2 radical in the troposphere makes highly probable the interactions of this species with the various RO_2 entities. We have included all of these reactions in the present master mechanism. It is recognized that in the next stage of development of simplified chemical reaction schemes some judicious choices of the most important RO_2 species will allow a dramatic limitation on the number of these reactions carried in the mechanism.

There are currently two experimental estimates of the rate constant for the reaction, $HO_2 + CH_3O_2 \rightarrow CH_3O_2H + O_2$. From molecular modulation spectrometry, CH_3O_2 and HO_2 were monitored directly by Cox and Tyndall (1980) in a Cl_2, CH_4, H_2, O_2 photochemical system. They reported:

$$k = 7.7(+18.4 \text{ or } -5.4) \times 10^{-14} \exp(1296 \pm 364)/T \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$$

over the range 275-338 K. At 298 K this gives $k = 6.0 \times 10^{-12}$, or the very wide range of values, 6.9×10^{-11} to 5.2×10^{-13} cm^3 $molec^{-1}$ s^{-1} with their stated uncertainty limits. In experiments of Kan et al. (1980) at 298 K, a value of 1.3×10^{-12} cm^3 $molec^{-1}$ s^{-1} was derived from the product rates determined using Fourier transform infrared analysis in the photooxidation of azomethane in varied amounts of oxygen gas. The Kan et al. values depend on the measured rates of CH_3O_2H and other products of the reactions and the choice for the rate constant function, $(k_a\ k_b)^{1/2}$, where k_a and k_b refer to the reactions:

a) $2\ HO_2 \rightarrow H_2O_2 + O_2$

b) 2 CH_3O_2 --> Products

k_a and k_b appear to be reasonably well established; see note 2 following Table I and the discussion of Atkinson and Lloyd related to k_b. Application of the geometric mean rule which seems to describe reasonably well many radical-radical reactions, $k_{ab} \cong 2(k_a\ k_b)^{1/2}$, gives for the rate constant of the CH_3O_2 + HO_2 reaction, k = 2.0 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}, in fair agreement with the estimate of Kan et al. Niki et al. (1982) estimated the rate constant, k_c = 1.5 (± 0.5) x 10^{-12} cm^3 $molec^{-1}$ s^{-1} for the analogous reaction of HO_2 with $C_2H_5O_2$:

c) $C_2H_5O_2$ + HO_2 --> $C_2H_5O_2H$ + O_2

On the basis of the current information on the HO_2-RO_2 reactions we have adopted a value of 1.5 x $10^{-12}$$cm^3$ $molec^{-1}$ s^{-1}, independent of temperature, for all the RO_2-HO_2 reactions. This lies within the uncertainty limits of all of the determinations, but obviously a very high uncertainty is associated with these rate constants. The choice of Atkinson and Lloyd for the HO_2-RO_2 rate constants is 3 x 10^{-12} cm^3 $molec^{-1}$ s^{-1}. The effect of using a higher number for the rate constant for the HO_2-RO_2 reactions is to make less important the HO_2-HO_2 reactions leading to H_2O_2, since a greater fraction of the radical termination is picked up by the RO_2 radicals which do not generate H_2O_2. It is evident that the importance of H_2O_2 in acid rain generation demands that we simulate its rate of generation with reasonable certainty. There is no question that more accurate estimates of the RO_2-HO_2

reactions are required to achieve this goal.

Also summarized in this section of the master mechanism are the reactions of formation and decay of the various peroxyacylnitrates (reactions 635-682), and the $RCOO_2$-NO and RO_2-NO reactions involving radicals formed from the various photochemical and free radical reactions of the carbonyl compounds.

vi. Reactions of the Hydroperoxides (reactions 771-980 in the Master Mechanism, Appendix A)

The major gas phase reactions which remove the organic hydroperoxides involve their photodecompositions and their reactions with HO-radicals. Studies related to only two members of the series, CH_3O_2H and $(CH_3)_3CO_2H$, have been reported, and the reactions of all of the other hydroperoxides must be estimated using these data. The photolysis of the hydroperoxides results largely in the cleavage of the RO--OH bond.

$$ROOH + h\nu \longrightarrow RO + HO$$

The RO_2H molecules absorb light in about the same region and with about the same absorption coefficient as H_2O_2. Reactions 771 through 868 give the authors' best estimate of the overall reactions which result from the photodecomposition of the various hydroperoxides involved in the master mechanism. The alkoxy radicals (RO) formed in the primary process react with oxygen or decompose by the several patterns which we have discussed in section III-C-ii-a; the reactions shown in the mechanism give the net products of the combined photodecomposition and the subsequent fast reaction of the RO species with oxygen.

The reaction of methylhydroperoxide (CH_3O_2H) with the HO-radical has been shown to involve H-atom abstraction from both the peroxide-end and the CH_3-group of the molecule (Niki et al., 1982):

a) $CH_3O_2H + HO \dashrightarrow CH_3O_2 + H_2O$

b) $CH_3O_2H + HO \dashrightarrow CH_2O_2H + H_2O$

For this particular molecule, the rates of the two reactive channels are about the same. Of course for the peroxides of greater molecular complexity, it is likely that the fraction of the reaction which occurs by the two channels will be somewhat different, and it is expected to be a function of the nature of the C-H bond on the C-atom attached to the $-O_2H$ group. Thus one would expect that the fraction of the reaction which occurs through the channel (b) will increase somewhat in the progression of molecules of the structure, CH_3O_2H, RCH_2O_2H, R_2CHO_2H, where R represents and organic group such as CH_3, C_2H_5, etc. Anastasi et al. (1978) suggest that the $t-C_4H_9OO--H$ bond is the reactive site for the HO attack on this peroxide molecule ($k \cong 3 \times 10^{-12}$ cm^3 $molec^{-1}$). However in the absence of definitive reaction rate data, an attempt to distinguish between the relative rates of the different reaction channels for these hydroperoxides is of questionable value at this time. For the higher molecular weight RO_2H molecules which have abstractable H-atoms on the carbon adjacent to the $-O_2H$ group, we will assume the same distribution of reaction in the two channels analogous to a) and b) above. This procedure follows the suggestion of Atkinson and Lloyd. It is understood that this can be only a gross approximation to the reactions of the higher molecular weight hydroperoxides, but in the absence of additional kinetic data, there is no more reasonable choice of action. For the peroxides in which the -OOH is attached to a tertiary-carbon atom, we make the logical assumption that only the abstraction of the H-atom on the -OOH group (reactive channel (a) above) occurs. All of the rate constants for the HO-radical attack on the RO_2H molecules (other than t-$C_4H_9O_2H$) are assumed equal to 1×10^{-11} cm^3 $molec^{-1}$ s^{-1} in accord with the estimate of Atkinson and Lloyd. The various HO-RO_2H reactions are shown in the master mechanism, Appendix A, reactions 869 through 980.

vii. The Chemistry of the Amines (reactions 981 through 1017 in the Master Mechanism, Appendix A)

The organic amines, like ammonia, are natural occurring basic compounds which can act to neutralize acids in the atmosphere, and their reactions should be considered in models built to describe acid generation in the troposphere. In the current master mechanism (Appendix A) we include the simplest members of this series of compounds, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, and $C_2H_5NH_2$. The major loss mechanisms which occur in the gas phase involve the HO-radical attack; in the case of the mono- and di-alkyl-group-substituted amines, attack occurs at both the C-H and N-H bond positions. E.g., with CH_3NH_2 the following reactions occur:

981a) $CH_3NH_2 + HO \rightarrow CH_2NH_2 + H_2O$

981b) $CH_3NH_2 + HO \rightarrow CH_3NH + H_2O$

The HO-radical-amine rate contants are from the studies of Atkinson et al. (1977,1978). The mechanism of the amine radical reactions and their rate constants given in the master mechanism were estimated from the relative rate data of Lindley et al. (1979) and by analogy with the measured rate constants for the reactions of NH_2 and the carbon species which is analogous to the amine species; e.g., $CH_2{=}NH$ is assumed to react with O_3 and HO-radicals with a rate constant equal to the corresponding reactions with $CH_2{=}CH_2$. Obviously these assignments are qualitative in nature, but they provide a useful framework on which to build our knowledge of these mechanisms until experimental or better theoretical estimates are available.

viii. Chlorine Chemistry (reactions 1018-1064 in the Master Mechanism, Appendix A)

The industrial release and generation of molecular chlorine through various atmospheric processes requires that serious consideration be given to the tropospheric reactions of Cl_2 which lead to acid generation, since the major product in which the chlorine eventually appears is the hydrogen chloride (HCl) molecule. Of course this forms the strong acid, hydrochloric acid, when it is incorporated into cloud water or surface waters. We have included Cl-atom reactions with the major inorganic trace species and all of the alkanes in the mechanism, the C_1- to C_5-aldehydes, and the C_2- to C_4-alkenes. (See Atkinson and Aschmann, 1984.)

ix. Summary

Although the master mechanism for the gas phase chemistry which we have described and presented in Appendix A appears to be rather extensive, it should be noted that only a small fraction of the total gas-phase tropospheric chemistry is represented by it. We have included only the important and representative impurity species which the available information suggests will affect acid generation in the troposphere. In the next stage of our planned effort, sensitivity studies should be made using the master mechanism, and the development of a simplified but scientifically realistic reaction scheme should be carried out. We consider the construction of the NCAR master mechanism to be far more than an academic exercise. It should be recognized that it is not scientifically sound to start with a simplified mechanism of acid generation of the troposphere without a thorough consideration of the many reactions pathways of the master mechanism. There is a significantly lower probablility of omission of some key reactions in the final simplified mechanism when the extended mechanism is an integral part of the final mechanism development.

The time frame for the development of the phase-one chemical module elements and the simultaneous planning for a state-of-the-art, scienticallly sound chemical module for final use in the acid deposition model, required our adopted two-channel effort related to the chemical modeling work. During the past year Drs. William R. Stockwell and Christopher J. Walcek have been working on the creation of a highly simplified gas-phase and liquid-phase model using a more empirical approach which was less time consuming and consistent with the schedule for the phase-one model development. The phase-one chemistry module will allow the necessary tests on the combined elements of the transport and transformation model, but we trust that improvements in the science of the chemistry mechanism will be possible as dictated by the more extensive scientific considerations carried out in this phase of the effort.

SECTION IV

THE MAJOR UNCERTAINTIES IN THE GAS-PHASE CHEMISTRY MECHANISM

It is evident that detailed sensitivity studies will be required to define well those reactions for which variations in the rate constant induce significant changes in the rates of acid generation. Professor Robert W. Carr, Jr., of the Department of Chemical Engineering and Materials Science, University of Minnesota, and his students will carry out some of these studies during the coming year (1985). However at this time it is possible to make a qualitative assessment of the rate constant and mechanism as outlined in the Appendix A and to identify the key reactions for which present kinetic data are inadequate and for which further experimental and theoretical studies are suggested. Each of the uncertainties bear upon the predictions of acid generation ($HONO_2$, H_2SO_4, HCO_2H, RCO_2H, CH_3SO_3H, NH_3, etc.). They relate to acid formation rates, either directly or indirectly, through their influence on O_3, HO, HO_2, RO_2, H_2O_2, and other species which control the acid generation in the gas-phase or liquid-phase reactions of the troposphere. Reference to the discussions of section III will provide the reader with additional background related to these recommendations.

A. The Inorganic Reactions

i) N_2O_5 and NO_3 Chemistry

The reactions of dinitrogen pentoxide and nitrogen trioxide can be very important sources of nitric acid during the nighttime hours. The recent literature shows a large divergence between the different experimental estimates of the equilibrium constant for the reactions, $N_2O_5 = NO_3 + NO_2$. For tropospheric conditions the largest share of the NO_3-radicals exist bound to NO_2 in the N_2O_5 molecule (greater than 90%), so that an error of a factor of two in this equilibrium constant will introduce very little error in the predicted $[N_2O_5]$ and its theoretical contribution to nitric acid generation on absorption into moist aerosols, fog, cloud, or rain water. On the other hand, the calculated concentration of the reactive NO_3-radical and the significance of nitric acid and peroxyacylnitrate formation through H-atom abstraction from the aldehydes are directly dependent on the value chosen for this equilibrium constant. It should be redetermined in experiments over the range of tropospheric temperatures in which all of the species are directly observed spectroscopically. Note that the present data have an uncertainty of a factor of two in all of the NO_3-radical reactions, and this can only be resolved with new and accurate measurements of the K_{eq}.

ii) The Atmospheric Chemistry of the HS-Free Radical

The rate constants for the reactions of HS with O_2 at atmospheric pressures are unknown today. In view of the catalytic role of O_3 destruction suggested for the HS-radical observed in low pressure experiments, it is important to test our chosen mechanism hypothesis ($HS + O_2 + M \rightarrow HSO_2 + M$; $HSO_2 + O_2 \rightarrow HO_2 + SO_2$) which is based solely on product studies at high pressures of air.

iii) The Atmospheric Chemistry of the NH_2-Free Radical

High uncertainties surround the reaction sequence of NH_2 decay in the troposphere. Although the apparent second order rate constant for the reaction 42, $NH_2 + O_2 (+M) \rightarrow NH_2O_2 (+M)$, is estimated to be less than 3×10^{-18} cm^3 $molec^{-1}$ s^{-1}, if k_{42} is near the experimentally determined upper limit, then reaction 42 is still the dominant reactive channel for the NH_2 radicals formed in the troposphere. One of the key unresolved questions which remains in the tropospheric gas-phase chemistry of the NH_2-free radical is whether NH_2 acts as a source of the reactive NO molecule through the reactions sequence 43, 44, 47-50, or whether it is a sink for active nitrogen through N_2O and/or N_2 formation in reactions 45 and 46. Although it is likely that NH_3 uptake by sulfuric acid aerosols is a dominant pathway for NH_3 removal for some tropospheric conditions, it could be a significnt source of NO for the tropospheric air masses which are relatively H_2SO_4-free.

iv) The Atmospheric Chemistry of Dimethylsulfide

The strong acid CH_3SO_3H can in theory contribute significantly to the natural acidity of cloud and rain water in regions of high natural emissions of CH_3SCH_3. Thus it is important that the mechanism of the CH_3SCH_3 reactions should be better defined so that the distribution of the expected CH_3SO_3H, SO_2, CH_3SNO, and CH_3SNO_2 products can be estimated with reasonable confidence.

B. The Hydrocarbon Chemistry

i) The Alkanes

The extensive studies of the reactions of the HO-radicals with the various hydrocarbons and their oxidation products now allow extrapolation of the existing data to derive realistic estimates of the HO-radical reactions with most of the hydrocarbons which are expected to be present in the troposphere. In our opinion the major uncertainties which dominate the detailed mechanisms of hydrocarbon oxidation relate to the reactions of the alkylperoxy and alkoxy radical reactions, the early products of the HO-hydrocarbon reaction sequence.

a) The RO_2-NO Reactions

The evidence for the partitioning of the products of the RO_2-NO reactions between the two channels (a) and (b) seems to be unambiguous.

a) $RO_2 + NO \rightarrow RO + NO_2$

b) $RO_2 + NO\ (+M) \rightarrow RONO_2\ (+M)$

However in view of the large effect which the inclusion of the reaction (b) has on O_3 development in simulations of tropospheric chemistry and the observed but unexpected temperature dependence of the rate constant for the class of the reactions represented by (b), it is important that these reactions be restudied, and the mechanism of the organic nitrate formation be confirmed by several independent laboratories.

b) The Reactions of the Long-Chain Alkoxy Radicals

The theoretical expectation that the internal abstraction mode is the major reaction of the long-chain ($>C_4$) alkoxy radicals must be tested through direct experimental observations of the products of some of these alkoxy radical systems (e.g., $CH_3CH_2CH_2CH_2O$).

ii) The Alkenes

a) Criegee Intermediates

Direct experimental estimates of the absolute rate constants of the reactions of the Criegee intermediates with NO, SO_2, NO_2, and H_2O are necessary to establish unambiguously the significance of these species in the tropospheric generation of sulfuric acid and organic acids.

b) The Beta-Hydroxy Alkoxy Radical Reactions

Studies of the unusual reactivity of the beta-hydroxy-substituted alkoxy radicals toward decomposition should be extended to the higher molecular weight radicals to establish the extent of this reactive channel compared to that forming carbonyl compounds and HO_2-free radicals. Our present estimates are based upon the quantitative observations from a single free radical species ($HOCH_2CH_2O$).

iii) The Aromatic Hydrocarbons

a) Mechanism of Tropospheric Oxidation

The available experimental data on the detailed mechanisms of the tropospheric oxidation of the aromatic hydrocarbons is very limited. The mass balance between the identified products and the reacted hydrocarbons are relatively poor for all of the aromatic hydrocarbons which have been studied. Although the loss rates for the these species and the extent of ozone generation observed in smog chamber experiments can be simulated reasonably well with the mechanisms adopted in the master mechanism of Appendix A, the present description of the product distribution is not well established experimentally and requires further study and amplification before any great confidence can be placed in the details of the mechanism and the specific influence of these species on the HO, HO_2, and RO_2 radical concentrations and acid production.

b) Vinyl-Peroxy and Phenyl-Peroxy Radical-NO_2 Reactions

Reactions such as 249, 285, etc., of the master mechanism have been proposed on the basis of the favorable thermochemistry alone; they have never been observed experimentally.

249) $C_6H_5O_2 + NO_2 \dashrightarrow C_6H_5O + NO_3$

285) $HCOCH{=}CHO_2 + NO_2 \dashrightarrow HCOCH(O_2)CHO + NO_3$

Obviously a definitive experimental evaluation of this type of "theoretical" reaction is necessary to anticipate its influence on $HONO_2$ generation in the troposphere.

iv) The Terpenes

As in the case of the aromatic hydrocarbons, the product distributions in the tropospheric oxidation of the terpenes is not well established. Product mass balances are relatively poor. More definitive work defining the nature of the products is imperative to establish the detailed reaction schemes and to derive the influence of the terpenes on the NO_x and SO_2 conversion to acids in the troposphere.

C. The Aldehyde and Ketone Chemistry

We have pointed out in the previous discussion in section III that the photochemical quantum yield data for the tropospheric conditions are not now available for 95% of the one-hundred or so carbonyl species which appear in the master mechanism. Many of the carbonyl compounds have been studied under conditions well removed from those of the troposphere (e.g., high concentrations of the carbonyl, little or no oxygen gas added, etc.). There is no sound theoretical basis for extrapolating these data to derive the necessary quantum yields for the dilute mixtures of the compounds in air, since oxygen and nitrogen gases can quench the excited states with efficiencies which are now unknown. Furthermore it is difficult to sort out from the laboratory experiments at high carbonyl compound concentrations, the true photolytic rates, since a correction of uncertain magnitude must be made to remove the rates of decay induced by free-radical attack on these compounds. It is recommended strongly that additional photochemical studies of the common carbonyl compounds be made under conditions which simulate the troposphere. We require a meaningful data base for the estimation of the primary quantum yields of these compounds which can be used to make reasonable extrapolations to the many carbonyl species involved in the master mechanism.

Particularly important in any newly planned photochemical studies is the estimation of quantum efficiencies as a function of wavelength, temperature, and pressure of air which cover the typical range of values encountered in the troposphere. Of course these studies should be made of those processes which generate free radical species, since the peroxy radicals which the free radicals generate help control the ozone levels and the extent of acid generation in the troposphere. However the intramolecluar primary processes of the larger ketones and aldehydes also are of major potential significance, since the reactive alkenes and enol-carbonyl compounds are the major products of these processes. Both species yield organic acids and peroxyacids upon reaction with ozone, and the Criegee intermediates formed can oxidize SO_2 to sulfuric acid.

It has been observed that acid rain generation and deposition is most significant during the summer months, and it seems reasonable to expect that this relates at least in part to the high sunlight intensity at this season and the rapid rate with which all of the photochemical processes are driven. It is clear that accurate experimental estimates of the rates of the photochemical processes must be obtained if a realistic treatment of these seemingly important processes is to be part of the acid generation and deposition models.

D. Radical-Radical Reactions

i) RO_2-HO_2 Reactions

In our previous discussions we noted that the organic hydroperoxides can oxidize HSO_3^- readily in aqueous solution to form sulfuric acid. Furthermore it was indicated that only two of the many hundreds of reactions which lead to these compounds have been studied kinetically (536 and 539), and even these data differ widely.

536) $CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2$

539) $C_2H_5O_2 + HO_2 \rightarrow C_2H_5O_2H + O_2$

The range of values for k_{536} extent from 1.3×10^{-12} to 6×10^{-12} $cm^3\ molec^{-1}\ s^{-1}$. It is very important to derive new, quantitative estimates of several of the related reactions involving hydroperoxides with a variety of structures so that a better confidence in the simulated rates of RO_2H generation can be had.

ii) Peroxyacylnitrate (PAN) Reactions

The only useful quantitative kinetic data available on the peroxyacylnitrates are those related to peroxyacetylnitrate ($CH_3COO_2NO_2$) and peroxybenzoylnitrate ($C_6H_5COO_2NO_2$). These data have been extrapolated to estimate the constants for the great number of the acylperoxy radical-NO_2 reactions (a) and the decomposition reactions of the many PAN species (b):

a) $RCOO_2 + NO_2 (+M) \dashrightarrow RCOO_2NO_2 (+M)$

b) $RCOO_2NO_2 (+M) \dashrightarrow RCOO_2 + NO_2 (+M)$

There are several reasons why the PAN's are of special concern to the modelers of tropospheric acid generation. The compound $CH_3COO_2NO_2$ has been shown to have a Henry's law constant of about 3 M atm^{-1} (22°C), and it is a good oxidant for HSO_3^{-1} ion in aqueous solution (Lee et al., 1983). The peroxyacylnitrates are believed to constitute a large fraction of the NO_x-containing compounds in the troposphere, and their decay reactions (b) may be a significant source of NO_2, as well as free radical and acid generation even during the nighttime hours. We recommend that the rate constants be determined experimentally for several of the higher homologues of PAN so that a more accurate treatment of the chemistry of these species can be given.

E. The Reactions of the Hydroperoxides

The quantum yields of the primary photochemical dissociation processes of the hydroperoxides are expected to be near unity, but only the simplest of these molecules has been studied experimentally. At least a few of the higher molecular weight hydroperoxides should be studied in synthetic air-rich mixtures so that we can have a better experimental basis for our quantum yield assignments.

Also important is the need for more extensive kinetic data on the HO-radical reactions with the organic hydroperoxides. Only data for CH_3O_2H and t-$C_4H_9O_2H$ exist now, and our extrapolation of this information to all other hydroperoxides must be of very limited accuracy. The reactions of the HO-radical with a number of the more complex hydroperoxides of a variety of molecular structures should be studied. Not only the rate constant for the initial H-atom abstraction is required, but a measure of the point of attack is important as well in order to derive the needed reaction mechanism for the modeling work.

F. Amine Chemistry

Most of the kinetic information related to the amine chemistry in the troposphere has been derived from a very few kinetic and mechanistic studies. The detailed decay reactions of these species include the generation of the nitrosamines (RN-N=O) and the nitramines ($RN-NO_2$) which are of special interest as cancer-inducing molecules. To what extent the amines either provide a source or a sink for NO_x in the atmosphere is now unclear. Studies to define better the reaction pathways are required to test and correct our current hypotheses.

G. The Validation of Tropospheric Acid Generation Mechanisms

It is surprising to find that there are very few experimental data which allow an adequate test of the detailed gas-phase mechanisms proposed to explain acid generation in the troposphere. Most existing data were obtained to test the mechanisms of oxidant generation in various hydrocarbon-NO_x mixtures in air; SO_2 was rarely included among the reactants in the mixtures. In the few experiments in which it was included, analyses of sulfuric acid, nitric acid, and the organic acids were usually not carried out. In smog chamber experiments, the rapid loss of $HONO_2$ at the wall is a serious problem, and the quantitative determination of H_2SO_4 aerosol involves different analytical techniques which complicate the usual experimental procedures which are employed (spectroscopic and gas chromatographic methods). Hydrogen peroxide (H_2O_2), thought to be the most important oxidant for HSO_3^- in cloud-water, has not been followed in smog chamber experiments. This is understandable since the loss of H_2O_2 at the walls of the chamber is probably as serious as that observed for $HONO_2$, and, furthermore, at the unrealistically high NO_x levels employed in most chamber experiments, little H_2O_2 is expected in theory.

New experimental tests of the rates of generation of the important acids, H_2SO_4, $HONO_2$, HCl, and the organic acids as well as the important oxidants, H_2O_2, CH_3O_2H, etc., in typical tropospheric mixtures of hydrocarbons, NO_x, and SO_2, should be developed in order to verify the schemes now employed and to allow their improvement. This is a very difficult if not impossible task if one depends on the use of the usual smog chambers. Some imaginative new methods which minimize wall interactions should be considered.

It is recognized that field measurements are expensive and difficult to make, but we should not accept any model which is developed until it has been tested against the experimental measurements (in the real atmosphere) of the key compounds related to acid generation. We consider here only the key species of the gas-phase mechanism. As a minimum check on the mechanism, simultaneous gas-phase measurements should be made on NO, NO_2, O_3, SO_2, H_2O_2, H_2O, CH_2O, CH_3CHO, PAN, $HONO_2$, a variety of the representative, major hydrocarbons, and aerosol amount and composition. The measurements should be made as a function of altitude and time of day and night for typical meteorological conditions encountered in the United States during different seasons of the year.

The authors know of no atmospheric measurements which have been made to date that include the necessary tropospheric reactants and products to test adequately any acid deposition model. Incomplete data sets (e.g., missing hydrocarbon, CH_2O, CH_3CHO, H_2O_2, etc.) which are available now should be used, of course, but they cannot provide the rigorous test of the models which is ultimately required.

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APPENDIX A

MASTER MECHANISM OF THE GAS PHASE CHEMISTRY

ADMP MODELING PROJECT

THE NATIONAL CENTER FOR ATMOSPHERIC RESEARCH

J. Alistair Kerr and Jack G. Calvert

(October 24, 1984)

APPENDIX A

MASTER MECHANISM OF THE GAS-PHASE CHEMISTRY

	Rate Constants k (cm^3, molec, sec, 298 K, 1 atm, 50% relative humidity)	E/R ,K
INORGANIC NO_x, HO_x, O_x, SO_2, H_2S, AND $(CH_3)_2S$ CHEMISTRY		
1) $NO_2 + hv \text{-->} NO + O(^3P)$	$J(NO_2)$	-----
2) $O(^3P) + O_2\ (+M) \text{-->} O_3$	1.5×10^{-14}	-5.6×10^2
3) $O_3 + NO \text{-->} NO_2 + O_2$	1.8×10^{-14}	1.37×10^3
4) $O(^3P) + NO_2 \text{-->} NO + O_2$	9.3×10^{-12}	0
5) $O(^3P) + NO_2\ (+M) \text{-->} NO_3$	1.6×10^{-12}	-4.2×10^2
6) $O_3 + NO_2 \text{-->} NO_3 + O_2$	3.2×10^{-17}	2.45×10^3
7) $NO_3 + NO \text{-->} 2NO_2$	2.0×10^{-11}	-----
8) $HO_2 + NO_2\ (+M) \text{-->} HO_2NO_2$	9.9×10^{-13}	-6.9×10^2
9) $HO_2NO_2\ (+M) \text{-->} HO_2 + NO_2$	5.3×10^{-2}	9.9×10^3
10) $NO_2 + HO\ (+M) \text{-->} HONO_2$	1.1×10^{-11}	-----
11) $HONO_2 + hv \text{-->} HO + NO_2$	$J(HONO_2)$	-----
12) $O_3 + HO \text{-->} HO_2 + O_2$	6.8×10^{-14}	9.4×10^2
13) $O_3 + HO_2 \text{-->} HO + 2O_2$	2.0×10^{-15}	5.8×10^2
14) $HO_2 + NO \text{-->} HO + NO_2$	8.3×10^{-12}	-2.4×10^2
15) $2HO_2\ (+M) \text{-->} H_2O_2 + O_2$	2.8×10^{-12}	(See Table 1 note)
16) $2HO_2 + H_2O\ (+M) \text{-->} H_2O_2 + O_2 + H_2O$	2.5×10^{-12}	(See Table 1)

17) O_3 + hv --> $O(^3P)$ + O_2	$J(O_3-^3P)$	-----
18) O_3 + hv --> $O(^1D)$ + O_2	$J(O_3-^1D)$	-----
19) $O(^1D)$ + O_2 --> $O(^3P)$ + O_2	4.0×10^{-11}	-6.7×10^1
20) $O(^1D)$ + N_2 --> $O(^3P)$ + N_2	2.6×10^{-11}	-1.1×10^2
21) $O(^1D)$ + H_2O --> 2HO	2.2×10^{-10}	0
22) NO + HO (+M) --> HONO	4.8×10^{-12}	-3.6×10^2
23) HONO + hv --> HO + NO	J(HONO)	-----
24) 2NO + O_2 --> $2NO_2$	$2.0 \times 10^{-38}[O_2]$	-5.3×10^2
25) NO_3 + NO_2 --> NO + NO_2 +O_2	4.0×10^{-16}	1.23×10^3
26) NO_3 + NO_2 (+M) --> N_2O_5	1.2×10^{-12}	6.0×10^1
27) N_2O_5 (+M) --> NO_3 + NO_2	5.2×10^{-2}	1.084×10^4
28) N_2O_5 + H_2O --> $2HONO_2$	0.0	-----
29) N_2O_5 + hv --> NO_3 + NO_2	$J(N_2O_5)$	-----
30) NO_3 + hv --> 0.11 NO + 0.89 NO_2 + 0.89 $O(^3P)$	$J(NO_3)$	-----
31) NO_2 + O_3 --> NO + $2O_2$	9.7×10^{-19}	2.45×10^3
32) NO_3 + M --> NO + O_2 + M	1.2×10^{-22}	6.84×10^3
33) NO_3 + HO_2 --> $HONO_2$ + O_2	2.5×10^{-12}	0(?)
34) H_2O_2 + HO --> H_2O + HO_2	1.7×10^{-12}	1.87×10^2
35) H_2O_2 + hv --> 2HO	$J(H_2O_2)$	-----
36) CO + HO (+M) --> HO_2 + CO_2	2.4×10^{-13}	0
37) HO + HONO --> H_2O + NO_2	6.6×10^{-12}	0(?)
38) HO + $HONO_2$ --> H_2O + NO_3	1.3×10^{-13}	-7.78×10^2
39) HO + HO_2NO_2 --> H_2O + NO_2 + O_2	4.6×10^{-12}	-3.8×10^2

40) $HO + NH_3 \rightarrow H_2O + NH_2$	1.6×10^{-13}	9.0×10^{2}
41) $NO_3 + NH_3 \rightarrow HONO_2 + NH_2$	?	?
42) $NH_2 + O_2$ (+M)$\rightarrow NH_2O_2$	$<3 \times 10^{-18}$	?
43) $NH_2O_2 + NH_2O_2 \rightarrow 2\ NH_2O + O_2$	?	?
44) $NH_2O_2 + NO \rightarrow NH_2O + NO_2$	7.6×10^{-12}?	-1.8×10^{2}?
45) $NH_2 + NO \rightarrow N_2 + H_2O$	1.6×10^{-11}	-4.5×10^{2}
46) $NH_2 + NO_2 \rightarrow N_2O + H_2O$	1.7×10^{-11}	-6.5×10^{2}
47) $NH_2 + O_3 \rightarrow NH_2O + O_2$	3.3×10^{-13}	1.15×10^{3}
48) $NH_2O + O_2 \rightarrow HNO + HO_2$	1.0×10^{-14}	2.9×10^{3}
49) HNO + hv --> HO_2 + NO	J(HNO)	-----
50) $HNO + O_2 \rightarrow HO_2 + NO$	$<2.1 \times 10^{-20}$	$>5.0 \times 10^{3}$
51) $HO + SO_2$ (+M) $\rightarrow HOSO_2$	1.1×10^{-12}	(See Table I note)
52) $HOSO_2 + O_2 \rightarrow SO_3 + HO_2$	4.0×10^{-13}	1.0×10^{3}
53) $O(^3P) + SO_2$ (+M) $\rightarrow SO_3$	3.4×10^{-14}	1.0×10^{3}
54) $SO_3 + H_2O$ (+M) $\rightarrow H_2SO_4$	9.1×10^{-13}	?
55) $HO + H_2S \rightarrow H_2O + HS$	4.7×10^{-12}	6.5×10^{1}
56) $NO_3 + H_2S \rightarrow HONO_2 + HS$	6.3×10^{-16}?	?
57) $HS + O_2$ (+M) $\rightarrow HSO_2$	?	?
58) $HS + O_2 \rightarrow HO_2 + S$	$<1 \times 10^{-17}$	?
59) $HSO_2 + O_2 \rightarrow HO_2 + SO_2$	?	?
60) $HS + O_3 \rightarrow HSO + O_2$	3.2×10^{-12}	?
61) $HS + NO_2$ (+M) $\rightarrow HSNO_2$(?)	3.0×10^{-11}	?
62) $HS + NO_2 \rightarrow HSO + NO$		
63) $HSO + O_3 \rightarrow SH + 2\ O_2$	1.0×10^{-13}	?

64) $HO + (CH_3)_2S \text{ --> } 0.x\ CH_3SCH_2O_2 + 0.x\ H_2O + 0.y\ CH_3S(OH)CH_3$	7.8×10^{-12}	-4.09×10^{2}
65) $NO_3 + (CH_3)_2S \text{ --> } 0.x\ HONO_2 + 0.x\ CH_3SCH_2O_2 + 0.y\ CH_3S(ONO_2)CH_3$	9.9×10^{-13}	6.0×10^{1}
66) $CH_3S(ONO_2)CH_3$ --> products?	?	?
67) $CH_3SCH_2O_2 + NO \text{ --> } CH_3SCH_2O + NO_2$	7.6×10^{-12}	-1.8×10^{2}
68) $CH_3SCH_2O + O_2 \text{ --> } CH_3SCHO + HO_2$	6×10^{-15}	7.5×10^{2}
69) $CH_3SCHO + hv \text{ --> } CH_3SO_2 + HO_2 + CO$	J(69)	-----
70) $CH_3SCH_2O \text{ --> } CH_3S + CH_2O$	?	?
71) $CH_3S + NO_2 \text{ --> } CH_3SNO_2$	3×10^{-11}?	?
72) $CH_3S + O_3 \text{ --> } CH_3SO + O_2$	3×10^{-12}?	?
73) $CH_3S + O_2\ (+M) \text{ --> } CH_3SOO$	$<10^{-17}$?	?
74) $CH_3S + NO\ (+M) \text{ --> } CH_3SNO$	6×10^{-11}?	?
75) $CH_3NO + hv \text{ --> } CH_3O_2 + NO$	J(75)	-----
76) $CH_3S + NO_2\ (+M) \text{ --> } CH_3SNO_2$	3×10^{-11}?	?
77) $CH_3SNO_2 + hv \text{ --> } CH_3S + NO_2$	J(77)	?
78) $CH_3SO + O_2 \text{ --> } CH_3SO_3$	?	?
79) $CH_3SO + O_3 \text{ --> } CH_3SO_2 + O_2$	?	?
80) $CH_3SOO\ (+M) \text{ --> } CH_3SO_2$	?	?
81) $CH_3SO_2\ (+M) \text{ --> } CH_3O_2 + SO_2$	2×10^{-1}?	1.0×10^{4}?
82) $CH_3SO_2 + O_3 \text{ --> } CH_3SO_3 + O_2$	?	?
83) $CH_3SO_3\ (+M) \text{ --> } CH_3O_2 + SO_3$	1×10^{-4}?	1.2×10^{4}?

84) $CH_3SO_3 + CH_2O \longrightarrow CH_3SO_3H + HO_2 + CO$	6×10^{-16}?	?
85) $CH_3SO_3 + CH_3CHO \longrightarrow CH_3SO_3H + CH_3COO_2$	2×10^{-15}?	?
86) $CH_3SO_3 + iso\text{-}C_4H_{10} \longrightarrow CH_3SO_3H + iso\text{-}C_4H_9O_2$	5.3×10^{-17}?	?
87) $CH_3S(OH)CH_3 + O_2 \longrightarrow CH_3S(OH)(O_2)CH_3$	?	?
88) $CH_3S(OH)CH_3 + O_2 \longrightarrow CH_3SOCH_3 + HO_2$	?	?
89) $CH_3S(OH)(O_2)CH_3 \longrightarrow CH_3SO_3H + CH_3O_2$	?	?
90) $CH_3S(OH)(O_2)CH_3 + NO \longrightarrow CH_3SO(OH)CH_3 + NO_2$	7.6×10^{-12}?	?
91) $CH_3SO(OH)CH_3 \longrightarrow CH_3SO(OH) + CH_3O_2$	?	?
92) $CH_3SO(OH)\ (+M) \longrightarrow CH_3O_2 + SO_2H$	?	?
93) $SO_2H + O_2 \longrightarrow HO_2 + SO_2$	?	?

THE HYDROCARBON CHEMISTRY

A. The Alkanes:

a) Methane Chemistry:

94) $CH_4 + HO \rightarrow CH_3O_2 + H_2O$	8.0×10^{-15}	1.71×10^3
95) $CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.6×10^{-12}	-1.8×10^2
96) $CH_3O + O_2 \rightarrow CH_2O + HO_2$	1.3×10^{-15}	1.31×10^3
97) $CH_3O + NO_2 \rightarrow CH_3ONO_2$	1.5×10^{-11}	0

(Some other reactions of the aldehydes, ketones, and the hydroperoxides and the alkoxy, alkylperoxy, and acylperoxy radicals derived from the photodecomposition of these compounds are given in later sections as well.)

b) Ethane Chemistry:

98) $C_2H_6 + HO \rightarrow C_2H_5O_2 + H_2O$	2.7×10^{-13}	1.26×10^3
99) $C_2H_5O_2 + NO \rightarrow C_2H_5O + NO_2$	7.6×10^{-12}	-1.8×10^2
100) $C_2H_5O + O_2 \rightarrow CH_3CHO + HO_2$	7.4×10^{-15}	6.5×10^2
101) $C_2H_5O + NO_2 \rightarrow C_2H_5ONO_2$	1.5×10^{-11}	0

c) Propane Chemistry:

102) $C_3H_8 + HO \rightarrow H_2O + 0.75\ i\text{-}C_3H_7O_2 + 0.25\ n\text{-}C_3H_7O_2$	1.2×10^{-12}	8.0×10^2
103) $n\text{-}C_3H_7O_2 + NO \rightarrow n\text{-}C_3H_7O + NO_2$	7.6×10^{-12}	-1.8×10^2
104) $i\text{-}C_3H_7O_2 + NO \rightarrow i\text{-}C_3H_7O + NO_2$	7.6×10^{-12}	-1.8×10^2
105) $n\text{-}C_3H_7O + O_2 \rightarrow C_2H_5CHO + HO_2$	7.4×10^{-15}	6.5×10^2
106) $i\text{-}C_3H_7O + O_2 \rightarrow CH_3COCH_3 + HO_2$	1.4×10^{-14}	2.3×10^2
107) $n\text{-}C_3H_7O + NO_2 \rightarrow n\text{-}C_3H_7ONO_2$	1.5×10^{-11}	0
108) $i\text{-}C_3H_7O + NO_2 \rightarrow i\text{-}C_3H_7ONO_2$	1.5×10^{-11}	0

i) n-Butane Chemistry:

109) $n\text{-}C_4H_{10} + HO \rightarrow H_2O + 0.86\ sec\text{-}C_4H_9O_2 + 0.14\ n\text{-}C_4H_9O_2$	2.6×10^{-12}	5.6×10^{2}
110) $n\text{-}C_4H_{10} + NO_3 \rightarrow HONO_2 + sec\text{-}C_4H_9O_2$	5.2×10^{-17}	?
111) $n\text{-}C_4H_9O_2 + NO \rightarrow n\text{-}C_4H_9O + NO_2$	7.0×10^{-12}	-1.8×10^{2}
112) $sec\text{-}C_4H_9O_2 + NO \rightarrow sec\text{-}C_4H_9O + NO_2$	7.0×10^{-12}	-1.8×10^{2}
113) $n\text{-}C_4H_9O_2 + NO \rightarrow n\text{-}C_4H_9ONO_2$	5.6×10^{-13}	-1.8×10^{2}
114) $sec\text{-}C_4H_9O_2 + NO \rightarrow sec\text{-}C_4H_9ONO_2$	5.6×10^{-13}	-1.8×10^{2}
115) $sec\text{-}C_4H_9O + NO_2 \rightarrow sec\text{-}C_4H_9ONO_2$	1.5×10^{-11}	0
116) $n\text{-}C_4H_9O + NO_2 \rightarrow n\text{-}C_4H_9ONO_2$	1.5×10^{-11}	0
117) $n\text{-}C_4H_9O + O_2 \rightarrow HO_2 + n\text{-}C_3H_7CHO$	4.4×10^{-15}	8.1×10^{2}
118) $n\text{-}C_4H_9O \rightarrow O_2CH_2CH_2CH_2CH_2OH$	5.7×10^{5}	3.9×10^{3}
119) $O_2CH_2CH_2CH_2CH_2OH + NO \rightarrow OCH_2CH_2CH_2CH_2OH + NO_2$	7.0×10^{-12}	-1.8×10^{2}
120) $O_2CH_2CH_2CH_2CH_2OH + NO \rightarrow O_2NOCH_2CH_2CH_2CH_2OH$	5.6×10^{-13}	0
121) $OCH_2CH_2CH_2CH_2OH \rightarrow HOCH_2CH_2CH_2CHOH$	2.7×10^{6}	3.3×10^{3}

122) $HOCH_2CH_2CH_2CHOH + O_2 \rightarrow HO_2 + HOCH_2CH_2CH_2CHO$	2×10^{-12}	?
123) sec-$C_4H_9O + O_2 \rightarrow CH_3COC_2H_5 + HO_2$	2.2×10^{-14}	1.2×10^{2}
124) sec-$C_4H_9O \rightarrow C_2H_5O_2 + CH_3CHO$	1.8×10^{3}	7.5×10^{3}

e) Isobutane Chemistry:

125) iso-$C_4H_{10} + HO \rightarrow H_2O +$ t-$C_4H_9O_2$	2.4×10^{-12}	3.9×10^{2}
126) iso-$C_4H_{10} + NO_3 \rightarrow HONO_2 +$ t-$C_4H_9O_2$	5.3×10^{-17}	?
127) t-$C_4H_9O_2 + NO \rightarrow$ t-$C_4H_9O + NO_2$	7.0×10^{-12}	-1.8×10^{2}
128) t-$C_4H_9O_2 + NO \rightarrow$ t-$C_4H_9ONO_2$	5.6×10^{-13}	-1.8×10^{2}
129) t-$C_4H_9O \rightarrow CH_3COCH_3 + CH_3O_2$	3.5×10^{3}	8.0×10^{3}
130) t-$C_4H_9O + NO_2 \rightarrow$ t-$C_4H_9ONO_2$	1.5×10^{-11}	0

f) 2,3-Dimethylbutane Chemistry:

131) $(CH_3)_2CHCH(CH_3)_2 + HO \rightarrow H_2O + 0.92(CH_3)_2CHC(O_2)(CH_3)_2 + 0.08(CH_3)_2CHCH(CH_3)CH_2O_2$	6.3×10^{-12}	-1.29×10^{2}
132) $(CH_3)_2CHCH(CH_3)_2 + NO_3 \rightarrow HONO_2 + (CH_3)_2CHC(O_2)(CH_3)_2$	2.2×10^{-16}	?
133) $(CH_3)_2CHCH(CH_3)CH_2O_2 + NO \rightarrow 0.83\ NO_2 + 0.83\ (CH_3)_2CHCH(CH_3)CH_2O + 0.17\ (CH_3)_2CHCH(CH_3)CH_2ONO_2$	7.6×10^{-12}	-1.8×10^{2}

134) $(CH_3)_2CHCH(CH_3)CH_2O + O_2$ --> $HO_2 + (CH_3)_2CHCH(CH_3)CHO$	1.3×10^{-14}	4.9×10^2
135) $(CH_3)_2CHCH(CH_3)CH_2O$ --> $O_2CH_2CH(CH_3)CH(CH_3)CH_2OH$	5.7×10^5	3.9×10^3
136) $O_2CH_2CH(CH_3)CH(CH_3)CH_2OH + NO$ --> 0.83 NO_2 + 0.83 $OCH_2CH(CH_3)CH(CH_3)CH_2OH$ + 0.17 $O_2NOCH_2CH(CH_3)CH(CH_3)CH_2OH$	7.6×10^{-12}	-1.8×10^2
137) $OCH_2CH(CH_3)CH(CH_3)CH_2OH$ --> 0.83 $HOCH_2CH(CH_3)CH(CH_3)CHOH$ + 0.17 $HOCH_2CH(CH_3)CH(CH_2O_2)CH_2OH$	3.2×10^6	3.3×10^3
138) $HOCH_2CH(CH_3)CH(CH_3)CHOH + O_2$ --> $HO_2 + HOCH_2CH(CH_3)CH(CH_3)CHO$	2×10^{-12}	0
139) $HOCH_2CH(CH_3)CH(CH_2O_2)CH_2OH + NO$ --> 0.83 NO_2 + 0.83 $HOCH_2CH(CH_3)CH(CH_2O)CH_2OH$ 0.17 $HOCH_2CH(CH_3)CH(CH_2ONO_2)CH_2OH$	7.6×10^{-12}	-1.8×10^2
140) $HOCH_2CH(CH_3)CH(CH_2O)CH_2OH$ --> 0.83 $HOCHCH(CH_3)CH(CH_2OH)_2$ + 0.17 $HOCH_2CH(CH_2O_2)CH(CH_2OH)_2$	3.2×10^6	3.3×10^3
141) $HOCHC(CH_3)CH(CH_2OH)_2 + O_2$ --> $HO_2 + HCOCH(CH_3)CH(CH_2OH)_2$	2×10^{-12}	0

142) $HOCH_2CH(CH_2O_2)CH(CH_2OH)_2$ + NO --> $0.83\ NO_2 + 0.83\ HO_2$ + $0.83\ (HOCH_2)_2CHCH(CH_2OH)CHO$ + $0.17\ HOCH_2CH(CH_2ONO_2)CH(CH_2OH)_2$	7.6×10^{-12}	-1.8×10^{2}
143) $(CH_3)_2CHC(O_2)(CH_3)_2$ + NO --> $0.83\ (CH_3)_2CHC(O)(CH_3)_2$ + $0.17\ (CH_3)_2CHC(ONO_2)(CH_3)_2$ + $0.83\ NO_2$	7.6×10^{-12}	-1.8×10^{2}
144) $(CH_3)_2CHC(O)(CH_3)_2$ --> $CH_3COCH_3 + i\text{-}C_3H_7O_2$	1.0×10^{4}	6.6×10^{3}

g) The Chemistry of the Higher Molecular Weight Alkanes:

145) C_5H_{12} + HO --> $C_5H_{11}O_2 + H_2O$	4.1×10^{-12}	5.3×10^{2}
146) C_6H_{14} + HO --> $C_6H_{13}O_2 + H_2O$	5.7×10^{-12}	5.3×10^{2}
147) C_7H_{16} + HO --> $C_7H_{15}O_2 + H_2O$	7.3×10^{-12}	5.3×10^{2}
148) C_8H_{18} + HO --> $C_8H_{17}O_2 + H_2O$	9.0×10^{-12}	5.3×10^{2}
149) $C_5H_{12} + NO_3$ --> $C_5H_{11}O_2$ + $HONO_2$	4.4×10^{-17}	?
150) $C_6H_{14} + NO_3$ --> $C_6H_{13}O_2$ + $HONO_2$	5.9×10^{-17}	?
151) $C_7H_{16} + NO_3$ --> $C_7H_{15}O_2$ + $HONO_2$	7.5×10^{-17}	?
152) $C_8H_{18} + NO_3$ --> $C_8H_{17}O_2$ + $HONO_2$	1.0×10^{-16}	?
153) $C_5H_{11}O_2$ + NO --> $C_5H_{11}O + NO_2$	6.8×10^{-12}	-1.8×10^{2}

154) $C_6H_{13}O_2 + NO \rightarrow C_6H_{13}O + NO_2$	6.3×10^{-12}	-1.8×10^{2}
155) $C_7H_{15}O_2 + NO \rightarrow C_7H_{15}O + NO_2$	5.9×10^{-12}	-1.8×10^{2}
156) $C_8H_{17}O_2 + NO \rightarrow C_8H_{17}O + NO_2$	5.8×10^{-12}	-1.8×10^{2}
157) $C_5H_{11}O_2 + NO \rightarrow C_5H_{11}ONO_2$	8.2×10^{-13}	-1.8×10^{2}
158) $C_6H_{13}O_2 + NO \rightarrow C_6H_{13}ONO_2$	1.3×10^{-12}	-1.8×10^{2}
159) $C_7H_{15}O_2 + NO \rightarrow C_7H_{15}ONO_2$	1.7×10^{-12}	-1.8×10^{2}
160) $C_8H_{17}O_2 + NO \rightarrow C_8H_{17}ONO_2$	1.8×10^{-12}	-1.8×10^{2}
161) $C_5H_{11}O + O_2 \rightarrow HO_2 +$ o.1 $n\text{-}C_4H_9CHO + 0.6\ n\text{-}C_3H_7COCH_3 + 0.3\ C_2H_5COC_2H_5$	1.5×10^{-14}	2.5×10^{2}
162) $C_6H_{13}O + O_2 \rightarrow HO_2 + C_5H_{12}(C{=}O)^{*}$	2.1×10^{-14}	1.7×10^{2}

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*This is a general formula representing the various isomeric C_6-aldehydes and ketones.

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163) $C_7H_{15}O + O_2 \rightarrow C_6H_{14}(C{=}O) + HO_2$	2.1×10^{-14}	1.5×10^{2}
164) $C_8H_{17}O + O_2 \rightarrow C_7H_{16}(C{=}O) + HO_2$	2.1×10^{-14}	1.4×10^{2}
165) $C_5H_{11}O \rightarrow C_5H_{10}(OH)O_2^{**}$	8.7×10^{5}	3.8×10^{3}

**This generalformula represents the various hydroxy, peroxy-radicals which are formed by self-abstraction of long-chain alkoxy radicals and subsequent reaction with O_2 (for example: $CH_3CH(O_2)CH_2CH_2CH_2OH$).

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166) $C_6H_{13}O \rightarrow C_6H_{12}(OH)O_2$	1.7×10^{6}	3.6×10^{3}
167) $C_7H_{15}O \rightarrow C_7H_{14}(OH)O_2$	2.4×10^{6}	4.3×10^{3}

168) $C_8H_{17}O$ --> $C_8H_{16}(OH)O_2$	2.7×10^6	3.3×10^3
169) $C_5H_{10}(OH)O_2$ + NO --> 0.89 NO_2 + 0.89 HO_2 + 0.89 $HOC_4H_9(C{=}O)$* 0.11 $C_5H_{10}(OH)ONO_2$**	7.6×10^{-12}	-1.8×10^2

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*This general formula signifies hydroxyketones of structures such as: $CH_3COCH_2CH_2CH_2CH_2OH$.

**This general formula signifies the hydroxyalkylnitrates of structures such as: $CH_3CH(ONO_2)CH_2CH_2CH_2OH$.

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170) $C_6H_{12}(OH)O_2$ + NO --> 0.83 NO_2 + 0.83 HO_2 + 0.83 $HOC_5H_{11}(C{=}O)$ 0.17 $C_6H_{12}(OH)ONO_2$	7.6×10^{-12}	-1.8×10^2
171) $C_7H_{14}(OH)O_2$ + NO --> 0.77 NO_2 + 0.77 HO_2 + 0.77 $HOC_6H_{13}(C{=}O)$ 0.23 $C_7H_{14}(OH)ONO_2$	7.6×10^{-12}	-1.8×10^2
172) $C_8H_{16}(OH)O_2$ + NO --> 0.76 NO_2 + 0.76 HO_2 + 0.76 $HOC_7H_{15}(C{=}O)$ 0.24 $C_8H_{16}(OH)ONO_2$	7.6×10^{-12}	-1.8×10^2

B. The Alkenes:

a) Ethylene Chemistry:

173) $CH_2{=}CH_2$ + HO --> $HOCH_2CH_2O_2$	8.4×10^{-12}	-8.39×10^0
174) $CH_2{=}CH_2$ + NO_3 --> $O_2CH_2CH_2ONO_2$	1.1×10^{-16}	?
175) $O_2CH_2CH_2ONO_2$ + NO --> NO_2 + $OCH_2CH_2ONO_2$	7.6×10^{-12}	-1.8×10^2

176) $OCH_2CH_2ONO_2 + O_2$ --> $HO_2 + ONO_2CH_2CHO$	6.2×10^{-15}	7.1×10^{2}
177) $OCH_2CH_2ONO_2$ --> $2\ CH_2O + NO_2$	1.1×10^{5}	5.8×10^{3}
178) $HOCH_2CH_2O_2 + NO$ --> $NO_2 + HOCH_2CH_2O$	7.6×10^{-12}?	-1.8×10^{2}
179) $HOCH_2CH_2O$ --> $2\ CH_2O + HO_2$	1.1×10^{5}	5.8×10^{3}
180) $HOCH_2CH_2O + O_2$ --> $HOCH_2CHO + HO_2$	6.2×10^{-15}	7.1×10^{2}
181) $CH_2{=}CH_2 + O_3$ --> $CH_2O + 0.4\ CH_2OO + 0.18\ CO_2 + 0.42\ CO + 0.12\ H_2 + 0.42\ H_2O + 0.12\ HO_2$	1.8×10^{-18}	2.6×10^{3}
182) $CH_2OO + NO$ --> $NO_2 + CH_2O$	7×10^{-12}	?
183) $CH_2OO + NO_2$ --> $NO_3 + CH_2O$	1.0×10^{-13}	?
184) $CH_2OO + SO_2$ --> $CH_2O + H_2SO_4$	7×10^{-12}	?
185) $CH_2OO + H_2O$ --> $HCO_2H + H_2O$	4×10^{-16}	?
186) $CH_2OO + CH_2O$ --> HCO_2CH_2OH	2×10^{-12}	?
187) $CH_2OO + CH_3CHO$ --> $CH_3CO_2CH_2OH$	2×10^{-12}	?
188) $HCO_2H + HO$ --> $H_2O + HO_2 + CO_2$	3.6×10^{-13}	7.7×10^{1}

b) Propylene Chemistry:

189) $CH_3CH{=}CH_2 + HO$ --> $0.65\ CH_3CH(O_2)CH_2OH + 0.35\ CH_3CH(OH)CH_2O_2$	2.9×10^{-11}	-5.4×10^{2}

190) $CH_3CH=CH_2$ + NO_3 --> $CH_3CH(O_2)CH_2ONO_2$	7.7×10^{-15}	?
191) $CH_3CH(O_2)CH_2ONO_2$ + NO --> 0.96 NO_2 + 0.96 $CH_3CH(O)CH_2ONO_2$ + 0.04 $CH_3CH(ONO_2)CH_2ONO_2$	7.6×10^{-12}	-1.8×10^{2}
192) $CH_3CH(O)CH_2ONO_2$ + O_2 --> HO_2 + $CH_3COCH_2ONO_2$	2.2×10^{-14}	1.2×10^{2}
193) $CH_3CH(O)CH_2ONO_2$ --> CH_3CHO + CH_2O + NO_2	1.8×10^{3}	7.5×10^{3}
194) $CH_3CH(O_2)CH_2OH$ + NO --> NO_2 + $CH_3CH(O)CH_2OH$	7.3×10^{-12}	-1.8×10^{2}
195) $CH_3CH(O)CH_2OH$ --> CH_3CHO + HO_2 + CH_2O	1.1×10^{5}	5.8×10^{3}
196) $CH_3CH(O)CH_2OH$ + O_2 --> CH_3COCH_2OH	6.2×10^{-15}	7.1×10^{2}
197) $CH_3CH(OH)CH_2O$ --> $CH_3CH(OH)O_2$ + CH_2O	0	-----
198) $CH_3CH(OH)CH_2O$ + O_2 --> HO_2 + $CH_3CH(OH)CHO$	6.2×10^{-15}	7.1×10^{2}
199) $CH_3CH(OH)CH_2O$ --> CH_2O + HO_2 + CH_3CHO	1.1×10^{5}	5.8×10^{3}
200) $CH_3CH(O_2)CH_2OH$ + NO --> $CH_3CH(ONO_2)CH_2OH$	2.9×10^{-13}	-1.8×10^{2}

201) $CH_3CH(OH)CH_2O_2 + NO \dashrightarrow NO_2 + HO_2 + CH_3CH(OH)CHO$	7.3×10^{-12}	-1.8×10^2
202) $CH_3CH(OH)CH_2O_2 + NO \dashrightarrow CH_3CH(OH)CH_2ONO_2$	2.9×10^{-13}	-1.8×10^2
203) $CH_3CH{=}CH_2 + O_3 \dashrightarrow 0.5\ CH_3CHO + 0.5\ CH_2O + 0.2\ CH_3CHOO + 0.33\ CO + 0.2\ HO_2 + 0.06\ CH_4 + 0.27\ CO_2 + 0.1\ OH + 0.22\ CH_3O_2 + 0.03\ CH_3O + 0.2\ CH_2OO + 0.06\ H_2 + 0.21\ H_2O$	1.1×10^{-17}	2.1×10^3
204) $CH_3CHOO + NO \dashrightarrow NO_2 + CH_3CHO$	7×10^{-12}	?
205) $CH_3CHOO + NO_2 \dashrightarrow NO_3 + CH_3CHO$	1.0×10^{-13}	?
206) $CH_3CHOO + H_2O \dashrightarrow CH_3CO_2H + H_2O$	4×10^{-16}	?
207) $CH_3CHOO + SO_2 \dashrightarrow CH_3CHO + H_2SO_4$	7×10^{-12}	?
208) $CH_3CHOO + CH_2O \dashrightarrow CH_3CO_2CH_2OH$	2×10^{-12}	?
209) $CH_3CHOO + CH_3CHO \dashrightarrow CH_3CO_2CH(CH_3)OH$	2×10^{-12}	?

c)Trans-2-Butene Chemistry:

210) $CH_3CH{=}CHCH_3 + HO \dashrightarrow CH_3CH(OH)CH(O_2)CH_3$	7.0×10^{-11}	-5.4×10^2
211) $CH_3CH{=}CHCH_3 + NO_3 \dashrightarrow CH_3CH(O_2)CH(ONO_2)CH_3$	3.9×10^{-13}	?

212)	$CH_3CH(O_2)CH(ONO_2)CH_3 + NO \text{-->} NO_2 + CH_3CH(O)CH(ONO_2)CH_3$	7.0×10^{-12}	-1.8×10^2
213)	$CH_3CH(O_2)CH(ONO_2)CH_3 + NO \text{-->} CH_3CH(ONO_2)CH(ONO_2)CH_3$	5.6×10^{-13}	-1.8×10^2
214)	$CH_3CH(O)CH(ONO_2)CH_3 + O_2 \text{-->} CH_3COCH(ONO_2)CH_3 + HO_2$	2.2×10^{-14}	1.2×10^2
215)	$CH_3CH(O)CH(ONO_2)CH_3 \text{-->} NO_2 + 2CH_3CHO$	1.7×10^2	?
216)	$CH_3CH(OH)CH(O_2)CH_3 + NO \text{-->} NO_2$ $CH_3CH(OH)CH(O)CH_3$	7.0×10^{-12}	-1.8×10^2
217)	$CH_3CH(OH)CH(O_2)CH_3 + NO \text{-->} CH_3CH(OH)CH(ONO_2)CH_3$	5.6×10^{-13}	-1.8×10^2
218)	$CH_3CH(OH)CH(O)CH_3 \text{-->} 2\ CH_3CHO + HO_2$	1.1×10^5	5.8×10^3
219)	$CH_3CH(OH)CH(O)CH_3 + O_2 \text{-->} CH_3CH(OH)COCH_3 + HO_2$	6.2×10^{-15}	7.1×10^2
220)	$CH_3CH{=}CHCH_3 + O_3 \text{-->} CH_3CHO + 0.4\ CH_3CHOO + 0.12\ CH_4$ $0.36\ CO_2 + 0.24\ CO + 0.29\ HO_2 + 0.19\ HO + 0.05\ CH_3O + 0.43\ CH_3O_2$	2.0×10^{-16}	1.1×10^3

d) Isobutene Chemistry:

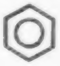
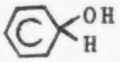
221)	$(CH_3)_2C{=}CH_2 + HO \text{-->} 0.x\ (CH_3)_2C(O_2)CH_2OH + 0.y\ (CH_3)_2C(OH)CH_2O_2$	5.1×10^{-11}	-5.0×10^2

222) $(CH_3)_2C=CH_2 + NO_3$ --> $(CH_3)_2C(O_2)CH_2ONO_2$	3.1×10^{-13}	?
223) $(CH_3)_2C(O_2)CH_2ONO_2 + NO$ --> $NO_2 + CH_3COCH_3 + CH_2O$	7.0×10^{-12}	-1.8×10^{2}
224) $(CH_3)_2C(O_2)CH_2ONO_2 + NO$ --> $(CH_3)_2C(ONO_2)CH_2ONO_2$	5.6×10^{-13}	-1.8×10^{2}
225) $(CH_3)_2C(O_2)CH_2OH + NO$ --> $NO_2 + CH_3COCH_3 +$ $+ HO_2 + CH_2O$	7.0×10^{-12}	-1.8×10^{2}
226) $(CH_3)_2C(O_2)CH_2OH + NO$ --> $(CH_3)_2C(ONO_2)CH_2OH$	5.6×10^{-13}	-1.8×10^{2}
227) $(CH_3)_2C(OH)CH_2O_2 + NO$ --> $NO_2 + (CH_3)_2C(OH)CH_2O$	7.0×10^{-12}	-1.8×10^{2}
228) $(CH_3)_2C(OH)CH_2O_2 + NO$ --> $(CH_3)_2C(OH)CH_2ONO_2$	5.6×10^{-13}	-1.8×10^{2}
229) $(CH_3)_2C(OH)CH_2O$ --> $CH_3COCH_3 +$ $HO_2 + CH_2O$	1.1×10^{5}	5.8×10^{3}
230) $(CH_3)_2C(OH)CH_2O + O_2$ --> $(CH_3)_2C(OH)CHO + HO_2$	7.4×10^{-15}	6.5×10^{2}
231) $(CH_3)_2C(OH)CHO + HO$ --> $H_2O +$ $(CH_3)_2C(OH)COO_2$	1.9×10^{-11}	-2.5×10^{2}
232) $(CH_3)_2C(OH)COO_2 + NO$ --> $NO_2 +$ $CO_2 + NO_2 + HO_2 + CH_3COCH_3$	1.0×10^{-11}	?

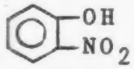
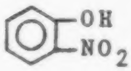
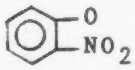
233) $(CH_3)_2C=CH_2 + O_3$ --> 0.5 CH_3COCH_3 + 0.2 CH_2OO + 0.2 $(CH_3)_2COO$ + 0.5 CH_2O + 0.43 CH_3O_2 + 0.36 CO_2 + 0.24 CO + 0.29 HO_2 + 0.19 HO + 0.05 CH_3O + 0.12 CH_4	1.2×10^{-17}	1.67×10^{3}
234) $(CH_3)_2COO + NO$ --> $CH_3COCH_3 + NO_2$	7×10^{-12}	?
235) $(CH_3)_2COO + NO_2$ --> $CH_3COCH_3 + NO_3$	1.0×10^{-13}	?
236) $(CH_3)_2COO + H_2O$ --> no reaction	0	
237) $(CH_3)_2COO + SO_2$ --> $CH_3COCH_3 + H_2SO_4$	7×10^{-12}	?
238) $(CH_3)_2COO + CH_2O$ --> $(CH_3)_2C(OH)OCHO$	2×10^{-12}	?
239) $(CH_3)_2COO + CH_3CHO$ --> $(CH_3)_2C(OH)OCOCH_3$	2×10^{-12}	?

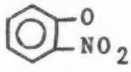
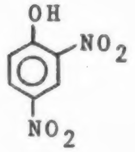
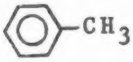
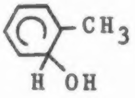
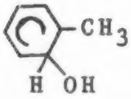
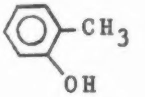
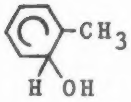
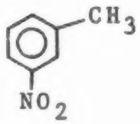
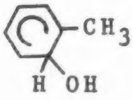
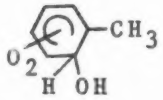
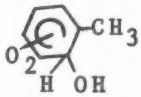
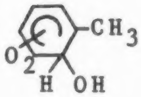
C. The Aromatic Hydrocarbons:

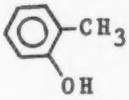
a) Benzene:

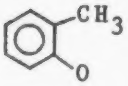
240)  + HO -->  (+O_2)--> NO_2 + HO_2 + $(HCO)_2$ + HCOCH=CHCHO	1.2×10^{-12}?	?

b) Toluene Chemistry

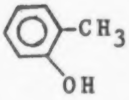
241) $C_6H_5CH_3 + HO \longrightarrow C_6H_5CH_2O_2 + H_2O$	5.1×10^{-13}	?
242) $C_6H_5CH_2O_2 + NO \longrightarrow C_6H_5CH_2O + NO_2$	6.3×10^{-12}	-1.8×10^{2}
243) $C_6H_5CH_2O + O_2 \longrightarrow C_6H_5CHO + HO_2$	1.1×10^{-14}	5.5×10^{2}
244) $C_6H_5CH_2O + NO_2 \longrightarrow C_6H_5CH_2ONO_2$	1.5×10^{-11}	?
245) $C_6H_5CH_2O_2 + NO \longrightarrow C_6H_5CH_2ONO_2$	7.0×10^{-13}	-1.8×10^{2}
246) $C_6H_5CHO + HO \longrightarrow C_6H_5COO_2 + H_2O$	1.2×10^{-11}	?
247) $C_6H_5COO_2 + NO \longrightarrow NO_2 + C_6H_5O_2 + CO_2$	7.6×10^{-12}	-1.8×10^{2}
248) $C_6H_5O_2 + NO \longrightarrow C_6H_5O + NO_2$	7.6×10^{-12}	-1.8×10^{2}
249) $C_6H_5O_2 + NO_2 \longrightarrow NO_3 + C_6H_5O$	6.0×10^{-12}?	?
250) $C_6H_5O + NO_2 \longrightarrow$ 	1.5×10^{-11}	?
251)  + NO_3 -->  + $HONO_2$	3.7×10^{-12}	?

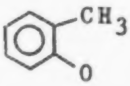
252)	 + NO_2 --> 	1.5 x 10^{-11}	?
253)	C_6H_5O + HO_2 --> C_6H_5OH + O_2	5.0 x 10^{-12}	?
254)	 + HO --> 	5.9 x 10^{-12}	-8.1 x 10^2
255)	 + O_2 -->  + HO_2	7 x 10^{-15}	5 x 10^2
256)	 + NO_2 -->  + H_2O	3 x 10^{-11}	?
257)	 + O_2 --> 	3.3 x 10^{-15}	?
258)	 + NO --> NO_2 + HO_2 + CH_3COCHO + HCOCH=CHCHO	7.6 x 10^{-12}	-1.8 x 10^2
259)	 + NO --> NO_2 + HO_2 $(HCO)_2$ + CH_3COCH=CHCHO	?	-----

260) 

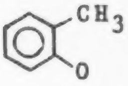
+ HO --> 

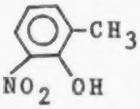
+ H_2O 3.3×10^{-12} 9.0×10^{2}

261) 

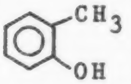
+ NO_3 --> 

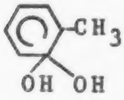
+ $HONO_2$ 2.2×10^{-11} ?

262) 

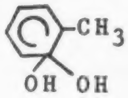
+ NO_2 --> 

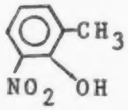
1.5×10^{-11} ?

263) 

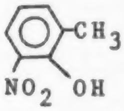
+ HO --> 

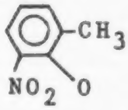
3.8×10^{-11} ?

264) 

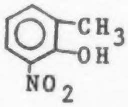
+ NO_2 --> 

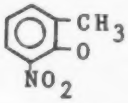
+ H_2O 3.1×10^{-11} ?

265) 

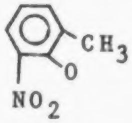
+ NO_3 --> 

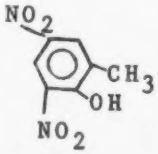
+ $HONO_2$ 2.2×10^{-11} ?

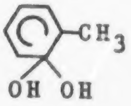
266) 

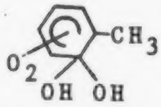
+ HO --> 

+ H_2O 3.8×10^{-11} ?

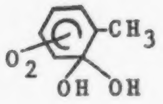
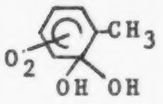
267) 

+ NO_2 --> 
NO2
CH3
OH
NO2
1.5×10^{-11} ?

268) 

+ O_2 --> 

3.3×10^{-15}? ?

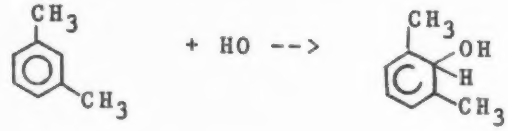
269)  + NO --> NO_2 + HO_2 + HCOCH=CHCHO + CH_3COCO_2H	7.6 x 10^{-12}	-1.8 x 10^{2}
270)  + NO --> NO_2 + HO_2 + CH_3COCH=CHCHO + $HCOCO_2H$	0 ?	?
271) $HCOCO_2H$ + HO --> H_2O + HO_2 + CO + CO_2	1.5 x 10^{-11}	?
272) $HCOCO_2H$ + NO_3 --> $HONO_2$ + CO + CO_2 + HO_2	2.5 x 10^{-15}	?
273) CH_3COCO_2H + HO --> H_2O + $O_2CH_2COCO_2H$	2.8 x 10^{-13}	?
274) $O_2CH_2COCO_2H$ + NO --> NO_2 + OCH_2COCO_2H	7.6 x 10^{-12}	-1.8 x 10^{2}
275) OCH_2COCO_2H + O_2 --> HO_2 + $HCOCOCO_2H$	7.4 x 10^{-15}	6.5 x 10^{2}
276) $HCOCOCO_2H$ + HO --> H_2O + 2CO + HO_2 + CO_2	1.7 x 10^{-11}	-2.5 x 10^{2}
277) $HCOCOCO_2H$ + NO_3 --> $HONO_2$ + 2 CO + CO_2 + HO_2	2.5 x 10^{-15}?	?
278) HCOCH=CHCHO + HO --> H_2O + HCOCH=$CHCOO_2$	3.0 x 10^{-11}	?
279) HCOCH=CHCHO + NO_3 --> $HONO_2$ + HCOCH=$CHCOO_2$	2.5 x 10^{-15}?	

280) $HCOCH{=}CHCOO_2 + NO \longrightarrow NO_2 + CO_2$ $HCOCH{=}CHO_2$	7.0×10^{-12}	-1.8×10^{2}
281) $HCOCH{=}CHO_2 + NO \longrightarrow NO_2 +$ $HCOCH(O_2)CHO$	7.3×10^{-12}	-1.8×10^{2}
282) $HCOCH(O_2)CHO + NO \longrightarrow$ $HCOCH(ONO_2)CHO$	2.9×10^{-13}	-1.8×10^{2}
283) $HCOCH(O_2)CHO + NO \longrightarrow (HCO)_2 +$ $NO_2 + HO_2 + CO$	7.3×10^{-12}	-1.8×10^{2}
284) $HCOCH{=}CHO_2 + NO \longrightarrow$ $HCOCH{=}CHONO_2$	2.9×10^{-13}	-1.8×10^{2}
285) $HCOCH{=}CHO_2 + NO_2 \longrightarrow$ $HCOCH(O_2)CHO + NO_3$	6.8×10^{-12} (0)?	?
286) $CH_3COCH{=}CHCHO + HO \longrightarrow H_2O +$ $CH_3COCH{=}CHCOO_2$	1.5×10^{-11}	?
287) $CH_3COCH{=}CHCHO + HO \longrightarrow$ $CH_3COCH(OH)CH(O_2)CHO$	5.0×10^{-12}	-5.0×10^{2}
288) $CH_3COCH{=}CHCHO + NO_3 \longrightarrow HONO_2$ $+ CH_3COCH{=}CHCOO_2$	2.5×10^{-15}?	?
289) $CH_3COCH(OH)CH(O_2)CHO + NO \longrightarrow$ $NO_2 + HO_2 + CH_3COCHO$ $(HCO)_2$	6.8×10^{-12}	-1.8×10^{2}
290) $CH_3COCH{=}CHCOO_2 + NO \longrightarrow NO_2 +$ $CO_2 + CH_3COCH{=}CHO_2$	1.0×10^{-11}	?
291) $CH_3COCH{=}CHO_2 + NO \longrightarrow NO_2$ $CH_3COCH(O_2)CHO$	7.0×10^{-12}	-1.8×10^{2}

292) $CH_3COCH(O_2)CHO + NO \text{ --> } CH_3COCH(ONO_2)CHO$	5.6×10^{-13}	-1.8×10^2
293) $CH_3COCH(O_2)CHO + NO \text{ --> } CH_3COCOCHO + HO_2 + NO_2$	7.0×10^{-12}	-1.8×10^2
294) $CH_3COCH{=}CHO_2 + NO \text{ --> } CH_3COCH{=}CHONO_2$	5.6×10^{-13}	-1.8×10^2
295) $CH_3COCH{=}CHO_2 + NO_2 \text{ --> } NO_3 + CH_3COCH(O_2)CHO$	6.0×10^{-12}	?
296) $CH_3COCH(O_2)(ONO_2) + NO \text{ --> } NO_2 + HO_2 + CH_3COCO_2NO_2$	7.3×10^{-12}	-1.8×10^2
297) $HCOCH(O_2)(ONO_2) + NO \text{ --> } NO_2 + HO_2 + HCOCO_2NO_2$	7.6×10^{-12}	-1.8×10^2
298) $CH_3COCH(ONO_2)CHO + HO \text{ --> } H_2O + CH_3COCH(ONO_2)COO_2$	1.9×10^{-11}	-2.5×10^2
299) $CH_3COCH(ONO_2)CHO + NO_3 \text{ --> } HONO_2 + CH_3COCH(ONO_2)COO_2$	2.5×10^{-15}?	?
300) $CH_3COCH(ONO_2)COO_2 + NO \text{ --> } CO_2 + NO_2 + CH_3COCH(O_2)(ONO_2)$	7.6×10^{-12}	-1.8×10^2
301) $HCOCH(ONO_2)CHO + HO \text{ --> } H_2O + HCOCH(ONO_2)COO_2$	1.7×10^{-11}	-2.5×10^2
302) $HCOCH(ONO_2)CHO + NO_3 \text{ --> } HONO_2 + HCOCH(ONO_2)COO_2$	2.5×10^{-15}	?
303) $HCOCH(ONO_2)COO_2 + NO \text{ --> } NO_2 + HCOCH(O_2)(ONO_2) + CO_2$	7.6×10^{-12}	-1.8×10^2

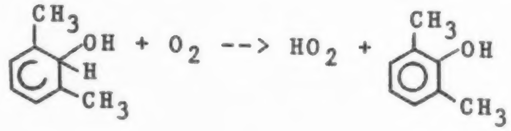
c) Meta-Xylene Chemistry:

304)


CH3
CH3
+ HO -->
CH3
OH
H
CH3

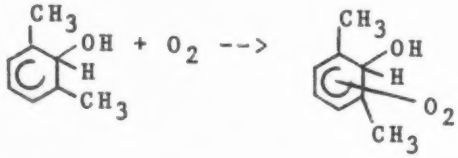
2.4×10^{-11} ?

305)


CH3
OH
H
CH3
+ O2 --> HO2 +
CH3
OH
CH3

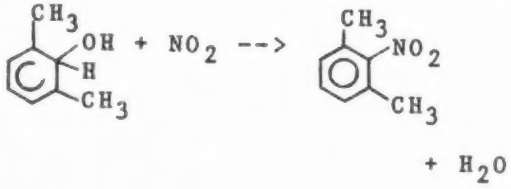
7×10^{-15} ?

306)


CH3
OH
H
CH3
+ O2 -->
CH3
OH
H
O2
CH3

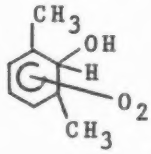
3.3×10^{-15} ?

307)


CH3
OH
H
CH3
+ NO2 -->
CH3
NO2
CH3
+ H2O

3.1×10^{-11} ?

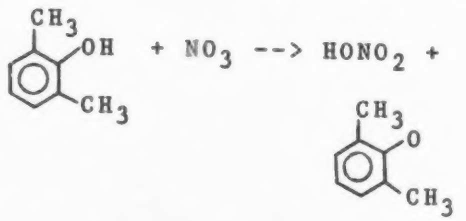
308)


CH3
OH
H
O2
CH3

$+ NO \rightarrow NO_2 + HO_2 + CH_3COCHO$
$+ 0.5\ CH_3COCH{=}CHCHO$
$+ 0.5\ CHOCH{=}C(CH_3)CHO$

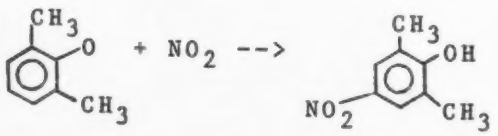
7.6×10^{-12}? -1.8×10^{2}

309)

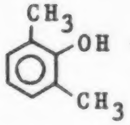
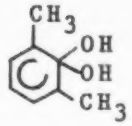

CH3
OH
CH3
+ NO3 --> HONO2 +
CH3
O
CH3

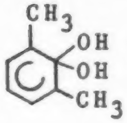
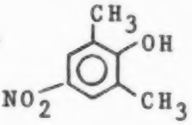
2.8×10^{-11} ?

310)

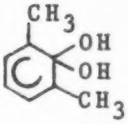
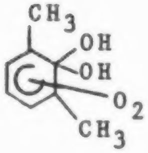

CH3
O
CH3
+ NO2 -->
CH3
OH
NO2
CH3

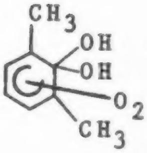
1.5×10^{-11} ?

311)  + HO -->  7×10^{-11} ?

312)  + NO_2 --> 

+ H_2O 3×10^{-11} ?

313)  + O_2 -->  3.3×10^{-15} ?

314)  + NO --> CH_3COCO_2H + 7.6×10^{-12} -1.8×10^2

NO_2 + 0.5$CH_3COCH{=}CHCHO$

+ HO_2 + 0.5$HCOCH{=}C(CH_3)CHO$

315) $HCOCH{=}C(CH_3)CHO$ + HO -->

$HCOCH(OH)C(O_2)(CH_3)CHO$ 5.0×10^{-12} ?

316) $HCOCH(OH)C(O_2)(CH_3)CHO$ + NO -->

+ 0.9 NO_2 + 0.9 $(HCO)_2$ +

0.9 CH_3COCHO + 0.9 HO_2 +

0.1 $HCOC(OH)CH(ONO_2)(CH_3)CHO$ 7.6×10^{-12} -1.8×10^2

317) $HCOCH{=}C(CH_3)CHO$ + HO --> H_2O +

$HCOCH{=}C(CH_3)COO_2$ 3.0×10^{-11}? ?

318) $HCOCH{=}C(CH_3)CHO$ + NO_3 -->

$HONO_2$ + $HCOCH{=}C(CH_3)COO_2$ 2.5×10^{-15}? ?

319) $HCOCH{=}C(CH_3)COO_2$ + NO --> NO_2

+ CO_2 + $HCOCH{=}C(CH_3)O_2$ 1.0×10^{-11}? ?

320) $HCOCH=C(CH_3)O_2 + NO \rightarrow NO_2 + CH_3COCH(O_2)CHO$	7.0×10^{-12}	-1.8×10^2
321) $HCOCH=C(CH_3)O_2 + NO_2 \rightarrow NO_3 + CH_3COCH(O_2)CHO$	6.8×10^{-12}?	?
322) $CH_3COCH(O_2)CHO + NO \rightarrow 0.93\ HO_2 + 0.1\ CO + 0.1\ CH_3COCHO + 0.07\ (HCO)_2 + NO_2 + 0.83\ CH_3COCOCHO$	7.0×10^{-12}	-1.8×10^2
323) $CH_3COCH(O_2)CHO + NO \rightarrow CH_3COCH(ONO_2)CHO$	5.6×10^{-13}	-1.8×10^2
324) $CH_3COCOCHO + HO \rightarrow H_2O + 2CO + CH_3COO_2$	1.9×10^{-11}	-2.5×10^2
325) $CH_3COCOCHO + NO_3 \rightarrow HONO_2 + CH_3COO_2 + 2\ CO$	2.5×10^{-15}	?

D. The Terpenes (Natural Hydrocarbons):

a)Isoprene:

326) $CH_2=C(CH_3)CH=CH_2 + HO \rightarrow + 0.x\ HOCH_2C(CH_3)(O_2)CH=CH_2 + 0.y\ CH_2=C(CH_3)CH(O_2)CH_2OH$	9.9×10^{-11}	-5.0×10^2
327) $HOCH_2C(CH_3)(O_2)CH=CH_2 + NO \rightarrow HO_2 + CH_2O + NO_2 + CH_3COCH=CH_2$	6.8×10^{-12}	-1.8×10^2
328) $HOCH_2C(CH_3)(O_2)CH=CH_2 + NO \rightarrow HOCH_2C(CH_3)(ONO_2)CH=CH_2$	8.2×10^{-13}	-1.8×10^2

329) $CH_2=C(CH_3)CH(O_2)CH_2OH + NO$ -->

$NO_2 + CH_2=C(CH_3)CHO + HO_2 + CH_2O$ 6.8×10^{-12} -1.8×10^2

330) $CH_2=C(CH_3)CH(O_2)CH_2OH + NO$ -->

$CH_2=C(CH_3)CH(ONO_2)CH_2OH$ 8.2×10^{-13} -1.8×10^2

331) $CH_2=C(CH_3)CH=CH_2 + O_3$ -->

$0.5\ CH_2O + 0.2\ CH_3COCH=CH_2 +$

$0.3\ CH_2=C(CH_3)CHO + 0.3\ CH_2OO +$

$0.06\ HO_2 + 0.2\ CO +$

$0.2\ CH_3C(OO)CH=CH_2 +$

$0.3\ CH_2=C(CH_3)CHOO + 0.34\ H_2O$ 1.1×10^{-17} 2.15×10^3

332) $CH_3C(OO)CH=CH_2 + NO$ --> NO_2 +

$CH_3COCH=CH_2$ 7×10^{-12} ?

333) $CH_3C(OO)CH=CH_2 + SO_2$ -->

$CH_3COCH=CH_2 + H_2SO_4$ 7×10^{-12} ?

334) $CH_3C(OO)CH=CH_2 + NO_2$ -->

$CH_3COCH=CH_2 + NO_3$ 1.0×10^{-13} ?

335) $CH_3C(OO)CH=CH_2 + H_2O$ --> H_2O +

no reaction 0 -----

336) $CH_3C(OO)CH=CH_2 + CH_2O$ -->

$CH_3C(OH)(OCHO)CH=CH_2$ 2×10^{-12} ?

337) $CH_3C(OO)CH=CH_2 + CH_3CHO$ -->

$CH_3C(OH)(OCOCH_3)CH=CH_2$ 2×10^{-12} ?

338) $CH_2=C(CH_3)CHOO + NO$ --> NO_2 +

$CH_3COCH=CH_2$ 7×10^{-12} ?

339) $CH_2=C(CH_3)CHOO + SO_2 \text{-->}$

$CH_3COCH=CH_2 + H_2SO_4$ 7×10^{-12} ?

340) $CH_2=C(CH_3)CHOO + NO_2 \text{-->}$

$CH_3COCH=CH_2 + NO_3$ 1.0×10^{-13} ?

341) $CH_2=C(CH_3)CHOO + H_2O \text{-->} H_2O$

$+ CH_2=C(CH_3)CO_2H$ 4×10^{-16} ?

342) $CH_2=C(CH_3)CHOO + CH_2O \text{-->}$

$CH_2=C(CH_3)CH(OH)OCHO$ 2×10^{-12} ?

343) $CH_2=C(CH_3)CHOO + CH_3CHO \text{-->}$

$CH_2=C(CH_3)CH(OH)OCOCH_3$ 2×10^{-12} ?

344) $CH_2=C(CH_3)CH=CH_2 + NO_3 \text{-->}$

$0.x\ O_2NOCH_2C(CH_3)(O_2)CH=CH_2$

$+ 0.y\ CH_2=C(CH_3)CH(O_2)CH_2ONO_2$ 5.9×10^{-13} ?

345) $O_2NOCH_2C(CH_3)(O_2)CH=CH_2 + NO \text{-->}$

$NO_2 + CH_2O + CH_3COCH=CH_2$ 6.8×10^{-12} -1.8×10^2

346) $O_2NOCH_2C(CH_3)(O_2)CH=CH_2 + NO \text{-->}$

$O_2NOCH_2C(CH_3)(ONO_2)CH=CH_2$ 8.2×10^{-13} -1.8×10^2

347) $CH_2=C(CH_3)CH(O_2)CH_2ONO_2 + NO \text{-->}$

$CH_2=C(CH_3)CH(ONO_2)CH_2ONO_2$ 8.2×10^{-13} -1.8×10^2

348) $CH_2=C(CH_3)CH(O_2)CH_2ONO_2 + NO \text{-->}$

$NO_2 + CH_2O + CH_2=C(CH_3)CHO$ 6.8×10^{-12} -1.8×10^2

349) $CH_2=C(CH_3)CH(O)CH_2ONO_2 + O_2 \text{-->}$

$HO_2 + CH_2=C(CH_3)COCH_2ONO_2$? ?

350) $CH_2=C(CH_3)CH(O)CH_2ONO_2 \text{-->} NO_2$

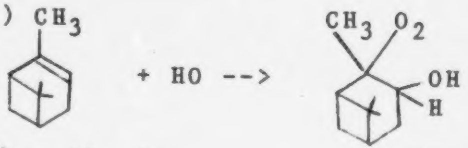
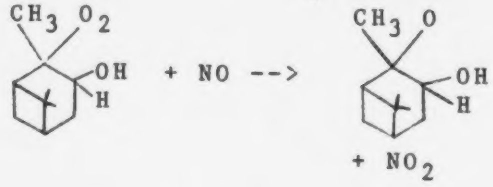
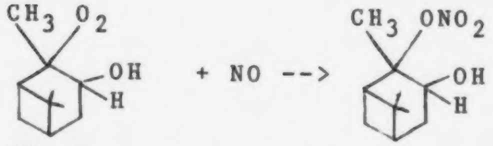
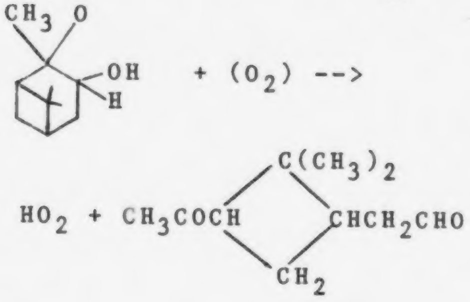
$+ CH_2O + CH_2=C(CH_3)CHO$? ?

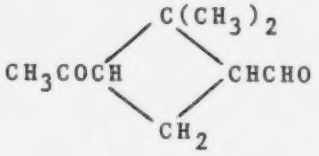
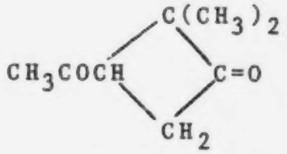
351) $CH_2{=}C(CH_3)CHO + HO \longrightarrow HOCH_2C(CH_3)(O_2)CHO$	1.02×10^{-11}	?
352) $HOCH_2C(CH_3)(O_2)CHO + NO \longrightarrow NO_2 + HO_2 + CH_2O + CH_3COCHO$	7.0×10^{-12}	-1.8×10^2
353) $HOCH_2C(CH_3)(O_2)CHO + NO \longrightarrow HOCH_2C(CH_3)(ONO_2)CHO$	5.6×10^{-13}	-1.8×10^2
354) $CH_2{=}C(CH_3)CHO + O_3 \longrightarrow 0.5\ CH_2O + 0.2\ CH_2OO + 0.5\ CH_3COCHO + 0.3\ HO_2 + 0.2\ CH_3C(OO)CHO + 0.35\ CO + 0.28\ CH_3CHO + 0.28\ CO_2$	1.1×10^{-18}	2.5×10^3
355) $CH_3C(OO)CHO + NO \longrightarrow NO_2 + CH_3COCHO$	7×10^{-12}	?
356) $CH_3C(OO)CHO + SO_2 \longrightarrow H_2SO_4 + CH_3COCHO$	7×10^{-12}	?
357) $CH_3C(OO)CHO + CH_2O \longrightarrow CH_3C(OH)(CHO)OCHO$	2×10^{-14}	?
358) $CH_3C(OO)CHO + CH_3CHO \longrightarrow CH_3C(OH)(CHO)OCOCH_3$	2×10^{-14}	?
359) $CH_2{=}C(CH_3)CHO + NO_3 \longrightarrow O_2NOCH_2C(CH_3)(O_2)CHO$	?	?
360) $O_2NOCH_2C(CH_3)(O_2)CHO + NO \longrightarrow 2\ NO_2 + CH_2O + CH_3COCHO$	7.0×10^{-12}	-1.8×10^2
361) $O_2NOCH_2C(CH_3)(O_2)CHO + NO \longrightarrow O_2NOCH_2C(CH_3)(ONO_2)CHO$	5.6×10^{-13}	-1.8×10^2

362) $CH_3COCH{=}CH_2 + O_3$ --> 0.5 CH_2O + 0.2 CH_2OO+ 0.5 CH_3COCHO + 0.2 $CH_3COCHOO^*$ + 0.36 HO_2 + + 0.28 CH_3CHO + 0.28 CO_2 + 0.35 CO	4.8×10^{-18}	2.0×10^{3}
363) $CH_3COCH{=}CH_2$ + HO --> $CH_3COCH(O_2)CH_2OH$	1.8×10^{-11}	-5.0×10^{2}
364) $CH_3COCH(O_2)CH_2OH$ + NO --> NO_2 + $CH_3COCH(O)CH_2OH$	7.0×10^{-12}	-1.8×10^{2}
365) $CH_3COCH(O_2)CH_2OH$ + NO --> $CH_3COCH(ONO_2)CH_2OH$	5.6×10^{-13}	-1.8×10^{2}
366) $CH_3COCH(O)CH_2OH + O_2$ --> $CH_3COCOCH_2OH + HO_2$	2.2×10^{-14}	1.2×10^{2}
367) $CH_3COCH(O)CH_2OH$ --> CH_3COCHO + $HO_2 + CH_2O$	1.1×10^{5}	5.8×10^{3}
368) $CH_3COCH{=}CH_2 + NO_3$ --> $CH_3COCH(O_2)CH_2ONO_2$	8×10^{-15}	?
369) $CH_3COCH(O_2)CH_2ONO_2$ + NO --> NO_2 $CH_3COCH(O)CH_2ONO_2$	7.0×10^{-12}	-1.8×10^{2}
370) $CH_3COCH(O_2)CH_2ONO_2$ + NO --> $CH_3COCH(ONO_2)CH_2ONO_2$	5.6×10^{-13}	-1.8×10^{2}
371) $CH_3COCH(O)CH_2ONO_2$ --> CH_3COCHO + $CH_2O + NO_2$	1.8×10^{3}	7.5×10^{3}
372) $CH_3COCH(O)CH_2ONO_2 + O_2$ --> HO_2 $CH_3COCOCH_2ONO_2$	2.2×10^{-14}	1.2×10^{2}

*[$CH_3C(OO)CHO$ is treated as $CH_3COCHOO$ for simplification.]

b) Alpha-Pinene:

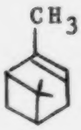
373)		5.6×10^{-11}	?
374)		7.2×10^{-12}	-1.8×10^{2}
375)		4.5×10^{-13}	-1.8×10^{2}
376)	 (R_1CHO)	3.5×10^{3}	8.0×10^{3}
377)	$R_1CHO + HO \rightarrow R_1COO_2 + H_2O$	1.9×10^{-11}	-2.5×10^{2}
378)	$R_1CHO + NO_3 \rightarrow HONO_2 + R_1COO_2$	2.5×10^{-15}?	?
379)	$R_1COO_2 + NO \rightarrow R_1O_2 + CO_2 + NO_2$	1.0×10^{-11}	?
380)	$R_1COO_2 + NO_2 \rightarrow R_1COO_2NO_2$	6×10^{-12}	0
381)	$R_1COO_2NO_2 \rightarrow NO_2 + R_1COO_2$	4×10^{-4}	1.3×10^{4}
382)	$R_1O_2 + NO \rightarrow R_1O + NO_2$	5.8×10^{-12}	-1.8×10^{2}
383)	$R_1O_2 + NO \rightarrow R_1ONO_2$	1.8×10^{-12}	-1.8×10^{2}

384)	$R_1O + O_2 \rightarrow HO_2 +$  (R_2CHO)	4.4×10^{-15}	8.1×10^{2}
385)	$R_2CHO + HO \rightarrow R_2COO_2 + H_2O$	1.9×10^{-11}	-2.5×10^{2}
386)	$R_2CHO + NO_3 \rightarrow R_2COO_2 + HONO_2$	2.5×10^{-15}?	?
387)	$R_2COO_2 \quad NO \rightarrow R_2O_2 + CO_2 + NO_2$	1.0×10^{-11}	?
388)	$R_2O_2 + NO \rightarrow R_2O + NO_2$	5.8×10^{-12}	-1.8×10^{2}
389)	$R_2O_2 + NO \rightarrow R_2ONO_2$	1.8×10^{-12}	-1.8×10^{2}
390)	$R_2O + O_2 \rightarrow HO_2 +$ 	1.4×10^{-14}	2.3×10^{2}
391)	$R_2O \rightarrow$ $CH_3COCH(CH_2CHO)C(CH_3)_2(O_2)$	1.8×10^{3}	7.5×10^{3}
392)	$CH_3COCH(CH_2CHO)C(CH_3)_2(O_2) + NO$ $\rightarrow NO_2 + CH_3COCH(CH_2CHO)C(CH_3)_2(O)$	7.6×10^{-12}	-1.8×10^{2}
393)	$CH_3COCH(CH_2CHO)C(CH_3)_2(O) \rightarrow$ $CH_3COCH(O_2)CH_2CHO + CH_3COCH_3$	3.5×10^{3}	8.0×10^{3}
394)	$CH_3COCH(O_2)CH_2CHO + NO \rightarrow NO_2$ $+ CH_3COCH(O)CH_2CHO$	7.6×10^{-12}	-1.8×10^{2}
395)	$CH_3COCH(O)CH_2CHO + O_2 \rightarrow$ $CH_3COCOCH_2CHO + HO_2$	2.2×10^{-14}	1.2×10^{2}

396) $CH_3COCH(O)CH_2CHO \rightarrow CH_3COCHO$

$+ O_2CH_2CHO$ 1.8×10^3 7.5×10^3

397)

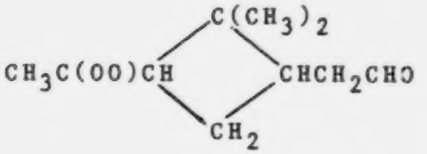


$+ O_3 \rightarrow 0.2\ X_1OO +$

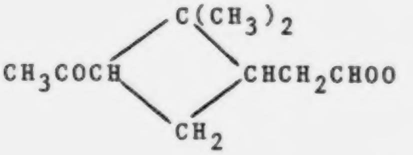
$0.2\ X_2OO + 0.3\ R_2O_2$

$+ 0.3\ CH_2O + 0.6\ HO_2$

$+ 0.3\ R_1O_2 + 0.3\ CO$ 8.1×10^{-17} 7.3×10^2



(X_1OO)



(X_2OO)

398) $X_1OO + NO \rightarrow R_1CHO + NO_2$ 7×10^{-12} ?

399) $X_1OO + SO_2 \rightarrow R_1CHO + H_2SO_4$ 7×10^{-12} ?

400) $X_1OO + CH_2O \rightarrow X_1(OH)OCHO$ 2×10^{-12} ?

401) $X_1OO + CH_3CHO \rightarrow X_1(OH)OCOCH_3$ 2×10^{-12} ?

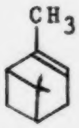
402) $X_2OO + NO \rightarrow X_2O + NO_2$ 7×10^{-12} ?

403) $X_2OO + SO_2 \rightarrow X_2O + H_2SO_4$ 7×10^{-12} ?

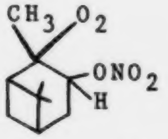
404) $X_2OO + CH_2O \rightarrow X_2(OH)OCHO$ 2×10^{-12} ?

405) $X_2OO + CH_3CHO \rightarrow X_2(OH)OCOCH_3$ 2×10^{-12} ?

406)



$+ NO_3 \rightarrow$



(YO_2) 6.3×10^{-12} ?

407) YO_2 + NO --> YO + NO_2	5.8×10^{-12}	-1.8×10^{2}
408) YO_2 + NO --> $YONO_2$	1.8×10^{-12}	-1.8×10^{2}
409) YO + (O_2) --> HO_2 + NO_2 + R_1CHO	3.5×10^{3}	8.0×10^{3}

THE ALCOHOLS

410) CH_3OH + HO --> CH_2O + HO_2 + H_2O	1.0×10^{-12}	-3.3×10^{2}
411) C_2H_5OH + HO --> CH_3CHO + HO_2 + H_2O	3.5×10^{-12}	-3.1×10^{2}

ADDITIONAL ALDEHYDE AND KETONE CHEMISTRY

412) CH_2O + hv --> H_2 + CO	J(CH_2O-I)	-----
413) CH_2O + hv --> 2HO_2 + CO	J(CH_2O-II)	-----
414) CH_2O + hv --> HC(OH)O_2	J(CH_2O-III)	-----
415) CH_3CHO + hv --> CH_3O_2 + HO_2 + CO	J(MeCHO)	-----
416) $HOCH_2CHO$ + hv --> 2 HO_2 + CH_2O + CO	J($HOCH_2CHO$)	-----
417) $HCOCO_2H$ + hv --> 2 HO_2 + CO + CO_2	J($HCOCO_2H$)	-----
418) $(HCO)_2$ + hv --> 0.15 CH_2O + 0.85 H_2 + 1.85 CO	J(HCOCHO-I)	-----
419) $(HCO)_2$ + hv --> HC(OH)OO + CO	J(HCOCHO-II)	-----
420) C_2H_5CHO + hv --> $C_2H_5O_2$ + HO_2 + CO	J(EtCHO)	-----
421) $HOCH_2CH_2CHO$ + hv --> $HOCH_2CH_2O_2$ + HO_2 + CO	J(421)	-----
422) $CH_3CH(OH)CHO$ + hv --> HO_2 + CO + $CH_3CH(OH)O_2$	J(422)	-----
423) $HCOCH{=}CHONO_2$ + hv --> HO_2 + CO + $O_2CH{=}CHONO_2$	J(423)	-----
424) CH_3COCHO + hv --> CH_3CHO + CO	J(MeCOCHO-I)	-----
425) CH_3COCHO + hv --> CH_3O_2 + $HCOCOO_2$	J(MeCOCHO-II)	-----

426)	CH_3COCHO + hv --> $CH_3C(OH)OO$ + CO	J(MeCOCHO-III)	-----
427)	$HCOCOCO_2H$ + hv --> CO + $HCOCO_2H$	J($HCOCOCO_2H$)	-----
428)	$HCOCH(ONO_2)CHO$ + hv --> HO_2 + CO + $HCOCH(O_2)(ONO_2)$	J(428)	-----
429)	CH_3COCH_3 + hv -- CH_3O_2 + CH_3COO_2	J(Me_2CO)	-----
430)	CH_3COCH_2OH + hv --> CH_3COO_2 + CH_2O + HO_2	J(430)	-----
431)	CH_3COCO_2H + hv --> CH_3CHO + CO_2	J($MeCOCO_2H$-I)	-----
432)	CH_3COCO_2H + hv --> CH_3COO_2 + HO_2 + CO_2	J($MeCOCO_2H$-II)	-----
433)	CH_3COCO_2H + hv --> CH_3O_2 + CO + HO_2 + CO_2	J($MeCOCO_2H$-III)	-----
434)	n-C_3H_7CHO + hv --> n-$C_3H_7O_2$ + HO_2 + CO	J(n-PrCHO-I)	-----
435)	n-C_3H_7CHO + hv --> $CH_2=CH_2$ + $CH_2=CH(OH)$	J(n-PrCHO-II)	-----
436)	$HOCH_2CH_2CH_2CHO$ + hv --> $HOCH_2CH_2CH_2O_2$ + HO_2 + CO	J(436)	-----
437)	$HOCH_2CH_2CH_2CHO$ + hv --> 2 $CH_2=CH(OH)$	J(437)	-----
438)	$CH_3COCH(ONO_2)CHO$ + hv --> HO_2 + $CH_3COCH(O_2)(ONO_2)$ + CO	J(438)	-----

439) $CH_3COCOCHO$ + hv --> CH_3COO_2 + HO_2 + 2CO	J(439)	-----
440) C_2H_5COCHO + hv --> $C_2H_5COO_2$ + HO_2 + CO	J(440)	-----
441) HCOCH=CHCHO + hv --> HO_2 + CO + $HCOCH{=}CHO_2$	J(441)	-----
442) i-C_3H_7CHO + hv --> i-$C_3H_7O_2$ + HO_2 + CO	J(i-PrCHO)	-----
443) $(CH_3)_2C(OH)CHO$ + hv --> $2HO_2$ + CO + CH_3COCH_3	J(443)	-----
444) $CH_2{=}C(CH_3)CHO$ + hv --> $CH_2{=}C(CH_3)(O_2)$ + HO_2 + CO	J(MeAcrolein)	-----
445) $CH_3COC_2H_5$ + hv --> CH_3COO_2 + $C_2H_5O_2$	J(Et_2CO)	-----
446) $CH_3COCH_2CH_2OH$ = hv --> CH_3COO_2 + $HOCH_2CH_2O_2$	J(446)	-----
447) $CH_3COCH(OH)CH_3$ + hv --> CH_3COO_2 + CH_3CHO + HO_2	J(447)	-----
448) $CH_3COCOCH_3$ + hv --> 2 CH_3COO_2	J(Ac_2-I)	-----
449) $CH_3COCOCH_3$ + hv --> CH_3O_2 + CO + CH_3COO_2	J(Ac_2-II)	-----
450) $CH_3COCOCH_2OH$ + hv --> CH_3O_2 + CO + $HOCH_2COO_2$	J($MeCOCOCH_2OH$-I)	-----

451) $CH_3COCOCH_2OH$ + hv --> CH_3COO_2
+ CO + $HOCH_2O_2$ J(MeCOCOCH$_2$OH-II) -----

452) $CH_3COCH{=}CH_2$ + hv --> CH_3COO_2
+ $CH_2{=}CHO_2$ J(MeCOCH=CH$_2$) -----

453) i-C_4H_9CHO + hv --> i-$C_4H_9O_2$
+ HO_2 + CO J(i-BuCHO-I) -----

454) i-C_4H_9CHO + hv --> $CH_3CH{=}CH_2$
+ $CH_2{=}CH(OH)$ J(i-BuCHO-II) -----

455) sec-C_4H_9CHO + hv -->
sec-$C_4H_9O_2$ + HO_2 + CO J(sec-BuCHO-I) -----

456) sec-C_4H_9CHO + hv -->
$CH_2{=}CH_2$ + $CH_3CH{=}CH(OH)$ J(sec-BuCHO-II) -----

457) n-C_4H_9CHO + hv --> n-$C_4H_9O_2$ +
HO_2 + CO J(n-BuCHO-I) -----

458) n-C_4H_9CHO + hv --> $CH_3CH{=}CH_2$
+ $CH_2{=}CH(OH)$ J(n-BuCHO-II) -----

459) n-$C_3H_7COCH_3$ + hv --> n-$C_3H_7O_2$ +
CH_3COO_2 J(n-PrCOMe-I) -----

460) n-$C_3H_7COCH_3$ + hv --> $CH_2{=}CH_2$ +
$CH_3C(OH){=}CH_2$ J(n-PrCOMe-II) -----

461) i-$C_3H_7COCH_3$ + hv --> i-$C_3H_7O_2$
+ CH_3COO_2 J(i-PrCOMe) -----

462) $C_2H_5COC_2H_5$ + hv --> $C_2H_5O_2$ +
$C_2H_5COO_2$ J(Et$_2$CO) -----

463) $CH_3COCH_2CH_2CH_2OH$ + hv -->

CH_3COO_2 + $HOCH_2CH_2CH_2O_2$ J(463) -----

464) $CH_3COCH_2CH_2CH_2OH$ + hv -->

CH_2=CH(OH) + $CH_3C(OH)$=CH_2 J(464) -----

465) $CH_3CH(OH)CH(CH_3)CHO$ + hv -->

$CH_3CH(OH)CH(O_2)CH_3$ + HO_2 + CO J(465) -----

466) $CH_3CH(OH)CH(CH_3)CHO$ + hv -->

CH_2=CH(OH) + CH_3CH=CH(OH) J(466) -----

467) $HOCH_2CH(CH_3)COCH_3$ + hv -->

$HOCH_2CH(CH_3)O_2$ + CH_3COO_2 J(467) -----

468) $CH_3COCH(OH)COCHO$ + hv -->

HO_2 + $HCOCOO_2$ + CH_3COHO J(468) -----

469) CH_3COCH=CHCHO + hv --> CH_3COO_2 +

HCOCH=CHO_2 J(469) -----

470) HCOCH=$C(CH_3)CHO$ + hv -->

HCOCH=$C(CH_3)(O_2)$ + HO_2 + CO J(470) -----

471) $HOC_4H_9(C=O)^*$ + hv --> $C_2H_5COO_2$ +

$CH_3CH(O_2)CH_2OH$ J(C_5-OH-carb-I) -----

472) $HOC_4H_9(C=O)^*$ + hv --> CH_2=CH(OH)

+ $CH_3C(OH)$=CH_2 J(C_5-OH-carb-II) -----

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*Thesereactions are representative of those expected for the photodecomposition of the hydroxyketones and hydroxyaldehydesof the generalized formula, $HOC_nH_{2n+1}(C=O)$.

473) $(CH_3)_2CHCH(CH_3)CHO$ + hv -->

$(CH_3)_2CHCH(CH_3)O_2$ + HO_2 + CO J(473) -----

474) $(CH_3)_2CHCH(CH_3)CHO$ + hv -->

$CH_3CH{=}CH_2$ + $CH_3CH{=}CH(OH)$ J(474) -----

475) $HOCH_2CH(CH_3)CH(CH_3)CHO$ + hv -->

$HOCH_2CH(CH_3)CH(CH_3)O_2$ + HO_2 + CO J(475) -----

476) $HOCH_2CH(CH_3)CH(CH_3)CHO$ + hv -->

2 $CH_3CH{=}CH(OH)$ J(476) -----

477) $HOCH_2CH(CH_3)CH(CH_2OH)CHO$ + hv -->

$HOCH_2CH(CH_3)CH(O_2)CH_2OH$ + HO_2 + CO J(477) -----

478) $HOCH_3CH(CH_3)CH(CH_2OH)CHO$ + hv -->

$CH_3CH{=}CH(OH)$ + $HOCH_2CH{=}CH(OH)$ J(478) -----

479) $C_5H_{12}(C{=}O)^*$ + hv --> $C_2H_5COO_2$ +

$n\text{-}C_3H_7O_2^*$ J(C_6-carbonyl-I) -----

480) $C_5H_{12}(C{=}O)$ + hv -->

$CH_3C(OH){=}CH_2$ + $CH_3CH{=}CH_2^*$ J(C_6-carbonyl-II) -----

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*These reactions are representative of those expected for the photodecomposition of the ketones and aldehydes of the generalized formula, $C_nH_{2n}O$.

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481) $HOC_5H_{11}(C{=}O)$ + hv --> $C_2H_5COO_2$

+ $CH_3CH(O_2)CH_2OH$ J(C_6-OH-carb-I) -----

482) $HOC_5H_{11}(C{=}O)$ + hv --> $CH_3CH{=}CH(OH)$

+ $CH_3C(OH){=}CH_2$ J(C_6-OH-carb-II) -----

483) $C_2H_5COCH_2CH_2CH_2OH$ + hv -->

$C_2H_5COO_2$ + $HOCH_2CH_2CH_2O_2$ J(483) -----

484) $C_2H_5COCH_2CH_2CH_2OH$ + hv -->

$C_2H_5C(OH)=CH_2 + CH_2=CH(OH)$ J(484) -----

485) $C_6H_{14}(C=O)$ + hv --> $C_2H_5COO_2$ +

n-$C_4H_9O_2$ J(C_7-carbonyl-I) -----

486) $C_6H_{14}(C=O)$ + hv --> $CH_3C(OH)=CH_2$

+ $(CH_3)_2C=CH_2$ J(C_7-carbonyl-II) -----

487) $HOC_6H_{13}(C=O)$ + hv --> n-$C_3H_7COO_2$

+ $CH_3CH(O_2)CH_2OH$ J(C_7-OH-carb-I) -----

488) $HOC_6H_{13}(C=O)$ + hv --> $CH_3CH=CH(OH)$

+ $CH_3C(OH)=CHCH_3$ J(C_7-OH-carb-II) -----

489) C_6H_5CHO + hv --> $C_6H_5COO_2 + HO_2$ J(PhCHO) -----

490) $C_7H_{16}(C=O)$ + hv --> n-$C_3H_7COO_2$

+ n-$C_4H_9O_2$ J(C_8-carbonyl-I) -----

491) $C_7H_{16}(C=O)$ + hv -->

$C_2H_5C(OH)=CH_2 + (CH_3)_2C=CH_2$ J(C_8-carbonyl-II) -----

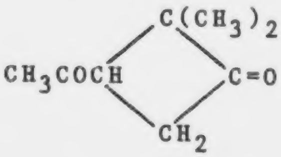
492) $HOC_7H_{15}(C=O)$ + hv --> n-$C_4H_9COO_2$

$CH_3CH(O_2)CH_2OH$ J(C_8-OH-carb-I) -----

493) $HOC_7H_{15}(C=O)$ + hv -->

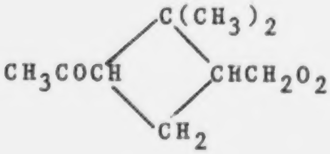
n-$C_3H_7CH=CH(OH) + CH_3C(OH)=CH_2$ J(C_8-OH-carb-II -----

494) R_2CHO + hv --> $R_2O_2 + HO_2 + CO$ J(R_2CHO) -----

495)  + hv -->

$CH_3COCH_3 + CH_3COCH=CH_2$

+ $CH_2O + CO_2$ J(495) -----

496) $CH_3COCOCH_2CHO$ + hv --> CO + HO_2 $CH_3COCOCH_2O_2$	J(496)	-----
497) $CH_3COC(CH_2CHO){=}C(CH_3)_2$ + hv --> $CH_3COC(CH_2O_2){=}C(CH_3)_2$ + HO_2 + CO	J(497)	-----
498) R_1CHO + hv -->  + HO_2 + CO (R_1O_2)	J(R_1CHO)	-----
499) CH_2O + HO --> HO_2 + CO + H_2O	1.0×10^{-11}	?
500) CH_3CHO + HO --> H_2O + CH_3COO_2	1.6×10^{-11}	-2.6×10^{2}
501) $HOCH_2CHO$ + HO --> H_2O +0.5 HO_2 0.5 $(HCO)_2$ + 0.5 $HOCH_2COO_2$	1.6×10^{-11}	-2.6×10^{2}
502) $(CHO)_2$ + HO --> H_2O + 2CO + HO_2	1.2×10^{-11}	?
503) C_2H_5CHO + HO --> H_2O + $C_2H_5COO_2$	1.9×10^{-11}?	-2.5×10^{2}?
504) $HOCH_2CH_2CHO$ + HO --> H_2O + $HOCH_2CH_2COO_2$	1.9×10^{-11}?	-2.5×10^{2}?
505) CH_3COCHO + HO --> H_2O + 0.x CO + 0.x CH_3COO_2 + 0.y CH_3COCOO_2	1.7×10^{-11}	-2.5×10^{2}?
506) i-C_3H_7CHO + HO --> H_2O + i-$C_3H_7COO_2$	1.9×10^{-11}?	-2.5×10^{2}?
507) n-C_3H_7CHO + HO --> H_2O + n-$C_3H_7COO_2$	2.5×10^{-11}?	-2.5×10^{2}?

508) $HOCH_2CH_2CH_2CHO + HO \text{ --> } H_2O + HOCH_2CH_2CH_2COO_2$	2.5×10^{-11}?	-2.6×10^{2}?
509) $n\text{-}C_4H_9CHO + HO \text{ --> } H_2O + n\text{-}C_4H_9COO_2$	1.6×10^{-11}?	-2.6×10^{2}?
510) $sec\text{-}C_4H_9CHO + HO \text{ --> } sec\text{-}C_4H_9COO_2$	1.6×10^{-11}?	-2.6×10^{2}?
511) $(CH_3)_2CHCH(CH_3)CHO + HO \text{ --> } (CH_3)_2CHCH(CH_3)COO_2 + H_2O$	1.6×10^{-11}?	-2.6×10^{2}?
512) $HOCH_2CH(CH_3)CH(CH_3)CHO + HO \text{ --> } HOCH_2CH(CH_3)CH(CH_3)COO_2 + H_2O$	1.6×10^{-11}?	-2.6×10^{2}?
513) $CH_3COCOCH_2CHO + HO \text{ --> } H_2O + CH_3COCOCH_2COO_2$	2.5×10^{-11}	-2.6×10^{2}
514) $CH_3COCH_3 + HO \text{ --> } CH_3COCH_2O_2 + H_2O$	2.8×10^{-13}	1.2×10^{3}
515) $CH_3COC_2H_5 + HO \text{ --> } H_2O + 0.84\ CH_3COCH(O_2)CH_3 + 0.16\ C_2H_5COCH_2O_2$	8.8×10^{-13}	?
516) $CH_2O + NO_3 \text{ --> } HONO_2 + HO_2 + CO$	6.3×10^{-16}	?
517) $CH_3CHO + NO_3 \text{ --> } HONO_2 + CH_3COO_2$	2.5×10^{-15}	?
518) $HOCH_2CHO + NO_3 \text{ --> } HONO_2 + HOCH_2COO_2$	2.5×10^{-15}	?
519) $C_2H_5CHO + NO_3 \text{ --> } HONO_2 + C_2H_5COO_2$	2.5×10^{-15}	?

520)	$HOCH_2CH_2CHO + NO_3 \longrightarrow HONO_2 + HOCH_2CH_2COO_2$	2.5×10^{-15}	?
521)	$i\text{-}C_3H_7CHO + NO_3 \longrightarrow HONO_2 + i\text{-}C_3H_7COO_2$	2.5×10^{-15}	?
522)	$n\text{-}C_3H_7CHO + NO_3 \longrightarrow HONO_2 + n\text{-}C_3H_7COO_2$	2.5×10^{-15}?	?
523)	$HOCH_2CH_2CH_2CHO + NO_3 \longrightarrow HONO_2 + HOCH_2CH_2CH_2COO_2$	2.5×10^{-15}	?
524)	$n\text{-}C_4H_9CHO + NO_3 \longrightarrow HONO_2$ $n\text{-}C_4H_9COO_2$	2.5×10^{-15}?	?
525)	$sec\text{-}C_4H_9CHO + NO_3 \longrightarrow HONO_2 + sec\text{-}C_4H_9COO_2$	2.5×10^{-15}?	?
526)	$i\text{-}C_4H_9CHO + NO_3 \longrightarrow HONO_2 + i\text{-}C_4H_9COO_2$	2.5×10^{-15}	?
527)	$CH_3COCOCH_2CHO + NO_3 \longrightarrow HONO_2 + CH_3COCOCH_2COO_2$	2.5×10^{-15}	?
528)	$(CH_3)_2CHCH(CH_3)CHO + NO_3 \longrightarrow (CH_3)_2CHCH(CH_3)COO_2 + HONO_2$	2.5×10^{-15}	?
529)	$HOCH_2CH(CH_3)CH(CH_3)CHO + NO_3 \longrightarrow HONO_2 + HOCH_2CH(CH_3)CH(CH_3)COO_2$	2.5×10^{-15}	?
530)	$CH_2O + HO_2 \longrightarrow O_2CH_2OH$	1.7×10^{-14}	?
531)	$O_2CH_2OH \longrightarrow CH_2O + HO_2$	1.5	?
532)	$O_2CH_2OH + NO \longrightarrow HCO_2H + NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^2

ADDITIONAL REACTIONS OF THE ALKOXY, ALKYLPEROXY, AND ACYLPEROXY RADICALS AND OTHER PRODUCTS OF THE ALDEHYDE REACTIONS

533) $2CH_3O_2$ --> $1.4\ CH_2O + 0.8\ HO_2 + 0.6\ CH_3OH + O_2$	3.4×10^{-13}?	2.2×10^2
534) $2C_2H_5O_2$ --> $1.58\ CH_3CHO + 0.44\ C_2H_5OH + O_2$	5.2×10^{-14} ?	5.0×10^2?
535) $CH_3O_2 + C_2H_5O_2$ --> $0.7\ CH_2O + 0.3\ CH_3OH + 0.4\ HO_2 + 0.79CH_3CHO + 0.22\ C_2H_5OH$	1.8×10^{-13}?	3.6×10^2
536) $CH_3O_2 + HO_2$ --> $CH_3O_2H + O_2$	1.5×10^{-12}	0
537) $O_2CH_2OH + HO_2$ --> $HO_2CH_2OH + O_2$	1.5×10^{-12}	0
538) $CH_2(Cl)(O_2) + HO_2$ --> $CH_2(Cl)(O_2H) + O_2$	1.5×10^{-12}	0
539) $C_2H_5O_2 + HO_2$ --> $C_2H_5O_2H + O_2$	1.5×10^{-12}	0
540) $CH_3CH(OH)O_2 + HO_2$ --> $CH_3CH(OH)O_2H + O_2$	1.5×10^{-12}	0
541) $HOCH_2CH_2O_2 + HO_2$ --> $HOCH_2CH_2O_2H + O_2$	1.5×10^{-12}	0
542) $HOCH_2CH(OH)O_2 + HO_2$ --> $HOCH_2CH(OH)O_2H + O_2$	1.5×10^{-12}	0
543) $CH_2{=}CHO_2 + HO_2$ --> $CH_2{=}CHO_2H + O_2$	1.5×10^{-12}	0
544) $O_2CH_2CHO + HO_2$ --> $HO_2CH_2CHO + O_2$	1.5×10^{-12}	0

545) $O_2CH_2CH_2ONO_2 + HO_2$ --> $HO_2CH_2CH_2ONO_2 + O_2$	1.5×10^{-12}	0
546) $HCOCH(O_2)(ONO_2) + HO_2$ --> $HCOCH(O_2H)(ONO_2) + O_2$	1.5×10^{-12}	0
547) $ClC_2H_4O_2 + HO_2$ --> $ClC_2H_4O_2H + O_2$	1.5×10^{-12}	0
548) $CH_3CH(Cl)(O_2) + HO_2$ --> $CH_3CH(Cl)(O_2H) + O_2$	1.5×10^{-12}	0
549) $i\text{-}C_3H_7O_2 + HO_2$ --> $i\text{-}C_3H_7O_2H + O_2$	1.5×10^{-12}	0
550) $HOCH_2CH_2CH_2O_2 + HO_2$ --> $HOCH_2CH_2CH_2O_2H + O_2$	1.5×10^{-12}	0
551) $n\text{-}C_3H_7O_2 + HO_2$ --> $n\text{-}C_3H_7O_2H + O_2$	1.5×10^{-12}	0
552) $CH_3COCH_2O_2 + HO_2$ --> $CH_3COCH_2O_2H + O_2$	1.5×10^{-12}	0
553) $CH_3C(OH)(O_2)CH_2OH + HO_2$ --> $CH_3C(OH)(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
554) $HOCH_2C(OH)(O_2)CH_2OH + HO_2$ --> $HOCH_2C(OH)(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
555) $CH_3CH(O_2)CH_2OH + HO_2$ --> $CH_3CH(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
556) $CH_3CH(OH)CH_2O_2 + HO_2$ --> $CH_3CH(OH)CH_2O_2H + O_2$	1.5×10^{-12}	0

557) $O_2CH_2COCO_2H + HO_2$ --> $HO_2CH_2COCO_2H + O_2$	1.5×10^{-12}	0
558) $HCOCH{=}CHO_2 + HO_2$ --> $HCOCH{=}CHO_2H + O_2$	1.5×10^{-12}	0
559) $HCOCH(O_2)CHO + HO_2$ --> $HCOCH(O_2H)CHO + O_2$	1.5×10^{-12}	0
560) $CH_2{=}C(CH_3)(O_2) + HO_2$ --> $CH_2{=}C(CH_3)(O_2H) + O_2$	1.5×10^{-12}	0
561) $CH_3CH(O_2)CH_2ONO_2 + HO_2$ --> $CH_3CH(O_2H)CH_2ONO_2 + O_2$	1.5×10^{-12}	0
562) $CH_3COCH(O_2)(ONO_2) + HO_2$ --> $CH_3COCH(O_2H)(ONO_2) + O_2$	1.5×10^{-12}	0
563) $ClC_3H_6O_2 + HO_2$ --> $ClC_3H_6O_2H + O_2$	1.5×10^{-12}	0
564) sec-$C_4H_9O_2 + HO_2$ --> sec-$C_4H_9O_2H + O_2$	1.5×10^{-12}	0
565) n-$C_4H_9O_2 + HO_2$ --> n-$C_4H_9O_2H + O_2$	1.5×10^{-12}	0
566) t-$C_4H_9O_2 + HO_2$ --> t-$C_4H_9O_2H + O_2$	1.5×10^{-12}	0
567) i-$C_4H_9O_2 + HO_2$ --> i-$C_4H_9O_2H + O_2$	1.5×10^{-12}	0
568) $CH_3COCH(O_2)CH_3 + HO_2$ --> $CH_3COCH(O_2H)CH_3 + O_2$	1.5×10^{-12}	0

569) $C_2H_5COCH_2O_2 + HO_2 \text{-->} C_2H_5COCH_2O_2H + O_2$	1.5×10^{-12}	0
570) $O_2CH_2CH_2CH_2CH_2OH + HO_2 \text{-->} HO_2CH_2CH_2CH_2CH_2OH + O_2$	1.5×10^{-12}	0
571) $HOCH_2C(OH)(O_2)CH(OH)CH_3 + HO_2 \text{-->} HOCH_2C(OH)(O_2H)CH(OH)CH_3 + O_2$	1.5×10^{-12}	0
572) $CH_3CH(OH)CH(O_2)CH_3 + HO_2 \text{-->} CH_3CH(OH)CH(O_2H)CH_3 + O_2$	1.5×10^{-12}	0
573) $C_2H_5C(OH)(O_2)CH_2OH + HO_2 \text{-->} C_2H_5C(OH)(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
574) $CH_3COCH{=}CHO_2 + HO_2 \text{-->} CH_3COCH{=}CHO_2H + O_2$	1.5×10^{-12}	0
575) $CH_3COCH(O_2)CHO + HO_2 \text{-->} CH_3COCH(O_2H)CHO + O_2$	1.5×10^{-12}	0
576) $CH_3COCOCH_2O_2 + HO_2 \text{-->} O_2 + CH_3COCOCH_2O_2H$	1.5×10^{-12}	0
577) $HOCH_2C(CH_3)(O_2)CHO + HO_2 \text{-->} HOCH_2C(CH_3)(O_2H)CHO + O_2$	1.5×10^{-12}	0
578) $O_2NOCH_2C(CH_3)(O_2)CHO + HO_2 \text{-->} O_2NOCH_2C(CH_3)(O_2H)CHO + O_2$	1.5×10^{-12}	0
579) $CH_3COCH(O_2)CH_2OH + HO_2 \text{-->} CH_3COCH(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
580) $HCOCH{=}C(CH_3)O_2 + HO_2 \text{-->} HCOCH{=}C(CH_3)O_2H + O_2$	1.5×10^{-12}	0

581) $CH_3COCH(O_2)CH_2ONO_2 + HO_2$ -->

$CH_3COCH(O_2H)CH_2ONO_2 + O_2$ 1.5×10^{-12} 0

582) $CH_3CH(O_2)CH(ONO_2)CH_3 + HO_2$ -->

$CH_3CH(O_2H)CH(ONO_2)CH_3 + O_2$ 1.5×10^{-12} 0

583) $(CH_3)_2C(O_2)CH_2OH + HO_2$ -->

$(CH_3)_2C(O_2H)CH_2OH + O_2$ 1.5×10^{-12} 0

584) $(CH_3)_2C(O_2)CH_2ONO_2 + HO_2$ -->

$(CH_3)_2C(O_2H)CH_2ONO_2 + O_2$ 1.5×10^{-12} 0

585) $CH_3CH(Cl)CH(O_2)CH_3 + HO_2$ -->

$CH_3CH(Cl)CH(O_2H)CH_3 + O_2$ 1.5×10^{-12} 0

586) $(CH_3)_2C(O_2)CH_2Cl + HO_2$ -->

$(CH_3)_2C(O_2H)CH_2Cl + O_2$ 1.5×10^{-12} 0

587) $C_5H_{11}O_2 + HO_2$ -->

$C_5H_{11}O_2H + O_2$ 1.5×10^{-12} 0

588) $(CH_3)_2CHCH(CH_3)O_2 + HO_2$ -->

$(CH_2)_2CHCH(CH_3)O_2H + O_2$ 1.5×10^{-12} 0

589) $HOCH_2CH(CH_3)CH(CH_3)O_2 + HO_2$ -->

$HOCH_2CH(CH_3)CH(CH_3)O_2H + O_2$ 1.5×10^{-12} 0

590) $CH_3COCH(OH)CH(O_2)CHO + HO_2$ -->

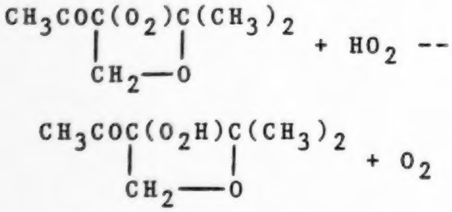
$CH_3COCH(OH)CH(O_2H)CHO + O_2$ 1.5×10^{-12} 0

591) $C_5H_{10}(OH)O_2 + HO_2 \longrightarrow C_5H_{10}(OH)O_2H + O_2$	1.5×10^{-12}	0
592) $HCOCH(OH)C(O_2)(CH_3)CHO + HO_2 \longrightarrow HCOCH(OH)C(O_2H)(CH_3)CHO + O_2$	1.5×10^{-12}	0
593) $HOCH_2C(CH_3)(O_2)CH{=}CH_2 + HO_2 \longrightarrow HOCH_2C(CH_3)(O_2H)CH{=}CH_2 + O_2$	1.5×10^{-12}	0
594) $CH_2{=}C(CH_3)CH(O_2)CH_2OH + HO_2 \longrightarrow CH_2{=}CH(CH_3)CH(O_2H)CH_2OH + O_2$	1.5×10^{-12}	0
595) $O_2CH_2CH(CH_3)CH(CH_3)OH + HO_2 \longrightarrow HO_2CH_2CH(CH_3)CH(CH_3)OH + O_2$	1.5×10^{-12}	0
596) $O_2NOCH_2C(CH_3)(O_2)CH{=}CH_2 + HO_2 \longrightarrow O_2NOCH_2C(CH_3)(O_2H)CH{=}CH_2 + O_2$	1.5×10^{-12}	0
597) $CH_2{=}CH(CH_3)CH(O_2)CH_2ONO_2 + HO_2 \longrightarrow CH_2{=}CH(CH_3)CH(O_2H)CH_2ONO_2 + O_2$	1.5×10^{-12}	0
598) $C_6H_{13}O_2 + HO_2 \longrightarrow C_6H_{13}O_2H + O_2$	1.5×10^{-12}	0
599) $(CH_3)_2CHC(O_2)(CH_3)_2 + HO_2 \longrightarrow (CH_3)_2CHC(O_2H)(CH_3)_2 + O_2$	1.5×10^{-12}	0
600) $(CH_3)_2CHCH(CH_3)CH_2O_2 + HO_2 \longrightarrow (CH_3)_2CHCH(CH_3)CH_2O_2H + O_2$	1.5×10^{-12}	0
601) $HOCH_2CH(CH_3)CH(CH_2O_2)CH_2OH + HO_2 \longrightarrow HOCH_2CH(CH_3)CH(CH_2O_2H)CH_2OH + O_2$	1.5×10^{-12}	0

602) $HOCH_2CH(CH_2O_2)CH(CH_2OH)_2 + HO_2 \longrightarrow$
$HOCH_2CH(CH_2O_2H)CH(CH_2OH)_2 + O_2$ 1.5×10^{-12} 0

603) $C_6H_{12}(OH)O_2 + HO_2 \longrightarrow$
$C_6H_{12}(OH)O_2H + O_2$ 1.5×10^{-12} 0

604) $C_6H_5O_2 + HO_2 \longrightarrow C_6H_5O_2H + O_2$ 1.5×10^{-12} 0

605)

$CH_3CO\underset{\underset{CH_2 — }{|}}{C}(O_2)\underset{\underset{O}{|}}{C}(CH_3)_2 + HO_2 \longrightarrow$
$CH_3CO\underset{\underset{CH_2 —— }{|}}{C}(O_2H)\underset{\underset{O}{|}}{C}(CH_3)_2 + O_2$ 1.5×10^{-12} 0

606) $CH_3COC(CH_2O_2)=C(CH_3)_2 + HO_2 \longrightarrow$
$CH_3COC(CH_2O_2H)=C(CH_3)_2 + O_2$ 1.5×10^{-12} 0

607) $CH_3COCOCH_2OC(CH_3)_2O_2 + HO_2 \longrightarrow$
$CH_3COCOCH_2OC(CH_3)_2O_2H + O_2$ 1.5×10^{-12} 0

608) $C_7H_{15}O_2 + HO_2 \longrightarrow$
$C_7H_{15}O_2H + O_2$ 1.5×10^{-12} 0

609) $C_6H_5CH_2O_2 + HO_2 \longrightarrow C_6H_5CH_2O_2H$
$+ O_2$ 1.5×10^{-12} 0

610) $C_7H_{14}(OH)O_2 + HO_2 \longrightarrow$
$C_7H_{14}(OH)O_2H + O_2$ 1.5×10^{-12} 0

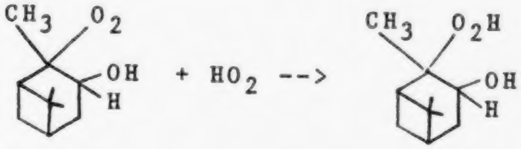
611) $C_8H_{17}O_2 + HO_2 \longrightarrow$
$C_8H_{17}O_2H + O_2$ 1.5×10^{-12} 0

612) $C_8H_{16}(OH)O_2 + HO_2 \longrightarrow$
$C_8H_{16}(OH)O_2H + O_2$ 1.5×10^{-12} 0

613) $R_1O_2 + HO_2 \longrightarrow R_1O_2H + O_2$ 1.5×10^{-12} 0

614) $R_2O_2 + HO_2 \longrightarrow R_2O_2H + O_2$ 1.5×10^{-12} 0

615) $YO_2 + HO_2 \rightarrow YO_2H + O_2$	1.5×10^{-12}	0
616) $CH_3COO_2 + HO_2 \rightarrow CH_3COO_2H + O_2$	1.5×10^{-12}	0
617) $HCOCOO_2 + HO_2 \rightarrow HCOCOO_2H + O_2$	1.5×10^{-12}	0
618) $C_2H_5COO_2 + HO_2 \rightarrow C_2H_5COO_2H + O_2$	1.5×10^{-12}	0
619) $CH_3COCOO_2 + HO_2 \rightarrow CH_3COCOO_2H + O_2$	1.5×10^{-12}	0
620) $HCOCH(ONO_2)COO_2 + HO_2 \rightarrow HCOCH(ONO_2)COO_2H + O_2$	1.5×10^{-12}	0
621) $i\text{-}C_3H_7COO_2 + HO_2 \rightarrow i\text{-}C_3H_7COO_2H + O_2$	1.5×10^{-12}	0
622) $n\text{-}C_3H_7COO_2 + HO_2 \rightarrow n\text{-}C_3H_7COO_2H + O_2$	1.5×10^{-12}	0
623) $(CH_3)_2C(OH)COO_2 + HO_2 \rightarrow (CH_3)_2C(OH)COO_2H + O_2$	1.5×10^{-12}	0
624) $HCOCH{=}CHCOO_2 + HO_2 \rightarrow HCOCH{=}CHCOO_2H + O_2$	1.5×10^{-12}	0
625) $CH_3COCH(ONO_2)COO_2 + HO_2 \rightarrow CH_3COCH(ONO_2)COO_2H + O_2$	1.5×10^{-12}	0
626) $sec\text{-}C_4H_9COO_2 + HO_2 \rightarrow sec\text{-}C_4H_9COO_2H + O_2$	1.5×10^{-12}	0
627) $n\text{-}C_4H_9COO_2 + HO_2 \rightarrow n\text{-}C_4H_9COO_2H + O_2$	1.5×10^{-12}	0

628) $i\text{-}C_4H_9COO_2 + HO_2$ --> $i\text{-}C_4H_9COO_2H + O_2$	1.5×10^{-12}	0
629) $CH_3COCH{=}CHCOO_2 + HO_2$ --> $CH_3COCH{=}CHCOO_2H + O_2$	1.5×10^{-12}	0
630) $HCOCH{=}C(CH_3)COO_2 + HO_2$ --> $HCOCH{=}C(CH_3)COO_2H + O_2$	1.5×10^{-12}	0
631) $C_6H_5COO_2 + HO_2$ --> $C_6H_5COO_2H + O_2$	1.5×10^{-12}	0
632) $R_1COO_2 + HO_2$ --> $R_1COO_2H + O_2$	1.5×10^{-12}	0
633) $R_2COO_2 + HO_2$ --> $R_2COO_2H + O_2$	1.5×10^{-12}	0
634)  + O_2	1.5×10^{-12}	0
635) $CH_3COO_2 + NO_2$ (+M) --> $CH_3COO_2NO_2$	6.0×10^{-12}	0
636) $CH_3COO_2NO_2$ (+M) --> $CH_3COO_2 + NO_2$	4.2×10^{-4}	1.33×10^{4}
637) $HOCH_2COO_2 + NO_2$ (+M) --> $HOCH_2COO_2NO_2$	6×10^{-12}	0
638) $HOCH_2COO_2NO_2$ (+M) --> $NO_2 + HOCH_2COO_2$	4×10^{-4}	1.3×10^{4}
639) $HCOCOO_2 + NO_2$ (+M) --> $HCOCOO_2NO_2$	6×10^{-12}	0

640) $HCOCOO_2NO_2$ (+M) --> NO_2 + $CHOCOO_2$	4×10^{-4}	1.3×10^{4}
641) $C_2H_5COO_2$ + NO_2 (+M) --> $C_2H_5COO_2NO_2$	6×10^{-12}	0
642) $C_2H_5COO_2NO_2$ (+M) --> NO_2 + $C_2H_5COO_2$	4×10^{-4}	1.3×10^{4}
643) $HOCH_2CH_2COO_2$ + NO_2 (+M) --> $HOCH_2CH_2COO_2NO_2$	6×10^{-12}	0
644) $HOCH_2CH_2COO_2NO_2$ (+M) --> NO_2 + $HOCH_2CH_2COO_2$	4×10^{-4}	1.3×10^{4}
645) $HCOCH(ONO_2)COO_2$ + NO_2 (+M) --> $HCOCH(ONO_2)COO_2NO_2$	6×10^{-12}	0
646) $HCOCH(ONO_2)COO_2NO_2$ (+M) --> $HCOCH(ONO_2)COO_2$ + NO_2	4×10^{-4}	1.3×10^{4}
647) CH_3COCOO_2 + NO_2 (+M) --> $CH_3COCOO_2NO_2$	6×10^{-12}	0
648) $CH_3COCOO_2NO_2$ (+M) --> NO_2 + CH_3COCOO_2	4×10^{-4}	1.3×10^{4}
649) i-$C_3H_7COO_2$ + NO_2 (+M) --> i-$C_3H_7COO_2NO_2$	6×10^{-12}	0
650) i-$C_3H_7COO_2NO_2$ (+M) --> NO_2 + i-$C_3H_7COO_2$	4×10^{-4}	1.3×10^{4}
651) n-$C_3H_7COO_2$ + NO_2 (+M) --> n-$C_3H_7COO_2NO_2$	6×10^{-12}	0

652) n-$C_3H_7COO_2NO_2$ (+M) --> NO_2 + n-$C_3H_7COO_2$	$4 \text{ x } 10^{-4}$	$1.3 \text{ x } 10^{4}$
653) $HOCH_2CH_2CH_2COO_2$ + NO_2 (+M) --> $HOCH_2CH_2CH_2COO_2NO_2$	$6 \text{ x } 10^{-12}$	0
654) $HOCH_2CH_2CH_2COO_2NO_2$ (+M) --> $HOCH_2CH_2CH_2COO_2$ + NO_2	$4 \text{ x } 10^{-4}$	$1.3 \text{ x } 10^{4}$
655) $HCOCH{=}CHCOO_2$ + NO_2 --> $HCOCH{=}CHCOO_2NO_2$	$6 \text{ x } 10^{-12}$	0
656) $HCOCH{=}CHCOO_2NO_2$ --> $HCOCH{=}CHCOO_2$ + NO_2	$4.2 \text{ x } 10^{-4}$	$1.3 \text{ x } 10^{4}$
657) $(CH_3)_2C(OH)COO_2$ + NO_2 (+M) --> $(CH_3)_2C(OH)COO_2NO_2$	$6 \text{ x } 10^{-12}$	0
658) $(CH_3)_2C(OH)COO_2NO_2$ (+M) --> $(CH_3)_2C(OH)COO_2$ + NO_2	$4 \text{ x } 10^{-4}$	$1.3 \text{ x } 10^{4}$
659) $CH_3COCOCH_2COO_2$ + NO_2 (+M) --> $CH_3COCOCH_2COO_2NO_2$	$6 \text{ x } 10^{-12}$	0
660) $CH_3COCOCH_2COO_2NO_2$ (+M) --> NO_2 + $CH_3COCOCH_2COO_2$	$4.2 \text{ x } 10^{-4}$	$1.33 \text{ x } 10^{4}$
661) $CH_3COCH(ONO_2)COO_2$ + NO_2 (+M) --> $CH_3COCH(ONO_2)COO_2NO_2$	$6 \text{ x } 10^{-12}$	0
662) $CH_3COCH(ONO_2)COO_2NO_2$ (+M) --> $CH_3COCH(ONO_2)COO_2$ + NO_2	$4 \text{ x } 10^{-4}$	$1.3 \text{ x } 10^{4}$
663) n-$C_4H_9COO_2$ + NO_2 (+M) --> n-$C_4H_9COO_2NO_2$	$6 \text{ x } 10^{-12}$	0

664) $n\text{-}C_4H_9COO_2NO_2$ (+M) --> $NO_2 + n\text{-}C_4H_9COO_2$	4×10^{-4}	1.3×10^{4}
665) $sec\text{-}C_4H_9COO_2 + NO_2$ (+M) --> $sec\text{-}C_4H_9COO_2NO_2$	6×10^{-12}	0
666) $sec\text{-}C_4H_9COO_2NO_2$ (+M) --> $NO_2 + sec\text{-}C_4H_9COO_2$	4×10^{-4}	1.3×10^{4}
667) $i\text{-}C_4H_9COO_2 + NO_2$ (+M) --> $i\text{-}C_4H_9COO_2NO_2$	6×10^{-12}	0
668) $i\text{-}C_4H_9COO_2NO_2$ (+M) --> $NO_2 + i\text{-}C_4H_9COO_2$	4×10^{-4}	1.3×10^{4}
669) $HCOCH{=}C(CH_3)COO_2 + NO_2$ (+M)--> $HCOCH{=}C(CH_3)COO_2NO_2$	6×10^{-12}	0
670) $HCOCH{=}C(CH_3)COO_2NO_2$ --> $NO_2 + HCOCH{=}C(CH_3)COO_2$	4×10^{-4}	1.3×10^{4}
671) $CH_3COCH{=}CHCOO_2 + NO_2$ --> $CH_3COCH{=}CHCOO_2NO_2$	6×10^{-12}	0
672) $CH_3COCH{=}CHCOO_2NO_2$ --> $NO_2 + CH_3COCH{=}CHCOO_2$	4×10^{-4}	1.3×10^{4}
673) $(CH_3)_2CHCH(CH_3)COO_2 + NO_2$ (+M) --> $(CH_3)_2CHCH(CH_3)COO_2NO_2$	6×10^{-12}	0
674) $(CH_3)_2CHCH(CH_3)COO_2NO_2$ (+M) --> $(CH_3)_2CHCH(CH_3)COO_2 + NO_2$	4×10^{-4}	1.3×10^{4}
675) $HOCH_2CH(CH_3)CH(CH_3)COO_2 + NO_2$ (+M) --> $HOCH_2CH(CH_3)CH(CH_3)COO_2NO_2$	6×10^{-12}	0

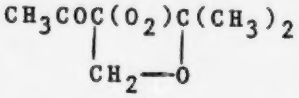
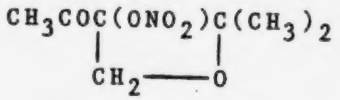
676) $HOCH_2CH(CH_3)CH(CH_3)COO_2NO_2$ (+M) --> $HOCH_2CH(CH_3)CH(CH_3)COO_2 + NO_2$	4×10^{-4}	1.3×10^{4}
677) $C_6H_5COO_2 + NO_2$ --> $C_6H_5COO_2NO_2$	6.0×10^{-12}	0
678) $C_6H_5COO_2NO_2$--> $C_6H_5COO_2 + NO_2$	1.8×10^{-4}	1.28×10^{4}
679) $R_2COO_2 + NO_2$ (+M) --> $R_2COO_2NO_2$	6×10^{-12}	0
680) $R_2COO_2NO_2$ (+M) --> NO_2 + R_2COO_2	4×10^{-4}	1.3×10^{4}
681) $R_1COO_2 + NO_2$ (+M) --> $R_1COO_2NO_2$	6×10^{-12}	0
682) $R_1COO_2NO_2$ (+M) --> NO_2 + R_1COO_2	4×10^{-4}	1.3×10^{4}
683) $CH_3COO_2 + NO$ --> $CH_3O_2 + NO_2 + CO_2$	1.0×10^{-11}	?
684) $HCOCOO_2 + NO$ --> $HO_2 + CO + NO_2 + CO_2$	1.0×10^{-11}	?
685) $CH_2{=}CHO_2 + NO$ --> $CH_2{=}CHO + NO_2$	7.6×10^{-12}	-1.8×10^{2}
686) $CH_2{=}CHO_2 + NO_2$ --> NO_3 + [$CH_2{=}CHO$ -->] O_2CH_2CHO	6×10^{-12}	0
687) $O_2CH_2CHO + NO$ --> $OCH_2CHO + NO_2$	7.6×10^{-12}	-1.8×10^{2}
688) $OCH_2CHO + O_2$ --> HO_2 + $(HCO)_2$	7.4×10^{-15}	6.5×10^{2}
689) $O_2CH{=}CHONO_2 + NO$ --> NO_2 + $(HCO)_2$	7.6×10^{-12}	-1.8×10^{2}

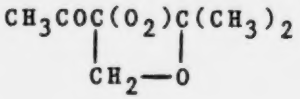
690) $HO + CH_2{=}CH(OH) \rightarrow HOCH_2CH(OH)O_2$	3×10^{-11}	-1.3×10^{1}
691) $HOCH_2CH(OH)O_2 + NO \rightarrow NO_2 + HOCH_2CH(OH)O$	7.6×10^{-12}	-1.8×10^{2}
692) $HOCH_2CH(OH)O \rightarrow HO_2 + CH_2O + HCO_2H$	1.1×10^{5}	5.8×10^{3}
693) $HOCH_2CH(OH)O + O_2 \rightarrow HOCH_2CO_2H + HO_2$	7.4×10^{-15}	6.5×10^{2}
694) $HOCH_2COO_2 + NO \rightarrow NO_2 + HO_2 + CO_2 + CH_2O$	1.0×10^{-11}	?
695) $C_2H_5COO_2 + NO \rightarrow C_2H_5O_2 + NO_2 + CO_2$	1.0×10^{-11}	?
696) $CH_3COCOO_2 + NO \rightarrow CH_3COO_2 + CO_2 + NO_2$	1.0×10^{-11}	?
697) $CH_3COCH_2O_2 + NO \rightarrow NO_2 + CH_3COCH_2O$	7.3×10^{-12}	-1.8×10^{2}
698) $CH_3COCH_2O_2 + NO \rightarrow CH_3COCH_2ONO_2$	2.9×10^{-13}	-1.8×10^{2}
699) $CH_3COCH_2O + O_2 \rightarrow HO_2 + CH_3COCHO$	6.9×10^{-16}	1.5×10^{3}
700) $CH_3COCH_2O \rightarrow CH_3COO_2 + CH_2O$	6.4×10^{2}?	?
701) $CH_2{=}C(CH_3)(O_2) + NO \rightarrow NO_2 + CH_3COCH_2O_2$	7.3×10^{-12}	-1.8×10^{2}

702) $CH_2=C(CH_3)(O_2)$ + NO_2 --> NO_3 + [$CH_2=C(CH_3)O$ -->] $CH_3COCH_2O_2$	6×10^{-12}	0
703) $HOCH_2CH_2CH_2O_2$ + NO --> NO_2 + $HOCH_2CH_2CH_2O$	7.3×10^{-12}	-1.8×10^2
704) $HOCH_2CH_2CH_2O_2$ + NO --> $HOCH_2CH_2CH_2ONO_2$	2.9×10^{-13}	-1.8×10^2
705) $HOCH_2CH_2CH_2O$ + O_2 --> HO_2 + $HOCH_2CH_2CHO$	7.4×10^{-15}	6.5×10^2
706) $C_2H_5COO_2$ + NO --> $C_2H_5O_2$ + CO_2 + NO_2	1.0×10^{-11}	?
707) $HOCH_2CH_2COO_2$ + NO --> NO_2 + CO_2 + $HOCH_2CH_2O_2$	1.0×10^{-11}	?
708) $HOCH_2CH(CH_3)O_2$ + NO --> $HOCH_2CH(CH_3)(O)$ + NO_2	7.6×10^{-12}	-1.8×10^2
709) $HOCH_2CH(CH_3)(O)$ + O_2 --> CH_3COCH_2OH + HO_2	1.4×10^{-14}	2.3×10^2
710) $CH_3CH=CH(OH)$ + HO --> $CH_3CH(O_2)CHO$ + 2 H_2O	7×10^{-11}	?
711) $CH_3CH(O_2)CHO$ + NO --> CH_3COCHO + HO_2 + NO_2	7.6×10^{-12}	-1.8×10^2
712) $CH_3COCH_2O_2$ + NO --> NO_2 + CH_3COCH_2O + NO_2 + HO_2	7.6×10^{-12}	-1.8×10^2
713) CH_3COCH_2O + O_2 --> HO_2 + CH_3COCHO	6.9×10^{-16}	1.4×10^3

714)	$CH_3COCH_2O + O_2 \longrightarrow CH_3COO_2 + CH_2O$	6.4×10^{2}	7.8×10^{3}
715)	$CH_3C(OH){=}CH_2 + HO \longrightarrow CH_3C(OH)(O_2)CH_2OH$	5.1×10^{-11}	-5.0×10^{2}
716)	$CH_3C(OH)(O_2)CH_2OH + NO \longrightarrow CH_3CO_2H + CH_2O + NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^{2}
717)	$CH_3COCOCH_2O_2 + NO \longrightarrow NO_2 + CH_3COCOCHO + HO_2$	7.6×10^{-12}	-1.8×10^{2}
718)	$i\text{-}C_3H_7COO_2 + NO \longrightarrow i\text{-}C_3H_7O_2 + NO_2 + CO_2$	1.0×10^{-11}	?
719)	$n\text{-}C_3H_7COO_2 + NO \longrightarrow n\text{-}C_3H_7O_2 + NO_2 + CO_2$	1.0×10^{-11}	?
720)	$CH_3COCH(O_2)CH_3 + NO \longrightarrow NO_2 + CH_3CH(O)COCH_3$	7.0×10^{-12}	-1.8×10^{2}
721)	$CH_3COCH(O_2)CH_3 + NO \longrightarrow CH_3COCH(ONO_2)CH_3$	5.6×10^{-13}	-1.8×10^{2}
722)	$C_2H_5COCH_2O_2 + NO \longrightarrow NO_2 + C_2H_5COCHO + HO_2$	7.6×10^{-12}	-1.8×10^{2}
723)	$CH_3CH(O)COCH_3 \longrightarrow CH_3CHO + CH_3COO_2$	1.6×10^{5}	6.4×10^{3}
724)	$CH_3CH(O)COCH_3 + O_2 \longrightarrow HO_2 + CH_3COCOCH_3$	2.2×10^{-15}	8.1×10^{2}
725)	$HOCH_2CH_2CH_2COO_2 + NO \longrightarrow NO_2 + CO_2 + HOCH_2CH_2CH_2O_2$	1.0×10^{-11}	?

726) $C_2H_5C(OH)=CH_2$ + HO --> $C_2H_5C(OH)(O_2)CH_2OH$	5.1×10^{-11}?	-5.0×10^{2}?
727) $C_2H_5C(OH)(O_2)CH_2OH$ + NO --> NO_2 + $C_2H_5CO_2H$ + HO_2 + CH_2O	7.6×10^{-12}	-1.8×10^{2}
728) $CH_3C(OH)=CHCH_3$ + HO --> $CH_3C(OH)(O_2)CH(OH)CH_3$	7×10^{-11}	?
729) $CH_3C(OH)(O_2)CH(OH)CH_3$ + NO --> CH_3CO_2H + $CH_3CH(OH)O_2$ + NO_2	7.0×10^{-12}	-1.8×10^{2}
730) $CH_3C(OH)(O_2)CH(OH)CH_3$ + NO --> $CH_3C(OH)(ONO_2)CH(OH)CH_3$	5.6×10^{-13}	-1.8×10^{2}
731) sec-$C_4H_9COO_2$ + NO --> NO_2 + CO_2 + sec-$C_4H_9O_2$	1.0×10^{-11}	?
732) n-$C_4H_9COO_2$ + NO --> NO_2 + CO_2 n-$C_4H_9O_2$	1.0×10^{-11}	?
733) i-$C_4H_9COO_2$ + NO --> NO_2 + CO_2 + i-$C_4H_9O_2$	1.0×10^{-11}	?
734) $(CH_3)_2CHCH(CH_3)O_2$ + NO --> $(CH_3)_2CHCH(CH_3)(O)$ + NO_2	7.0×10^{-12}	-1.8×10^{2}
735) $(CH_3)_2CHCH(CH_3)O_2$ + NO --> $(CH_3)_2CHCH(CH_3)ONO_2$	5.6×10^{-13}	-1.8×10^{2}
736) $(CH_3)_2CHCH(CH_3)(O)$ + O_2 --> i-$C_3H_7COCH_3$ + HO_2	2.2×10^{-14}	1.2×10^{2}
737) $(CH_3)_2CHCH(CH_3)(O)$ --> i-$C_3H_7O_2$ + CH_3CHO	2×10^{3}	7.5×10^{3}

738) $HOCH_2CH(CH_3)CH(CH_3)O_2 + NO \rightarrow HOCH_2CH(CH_3)CH(CH_3)(O) + NO_2$	6.8×10^{-12}	-1.8×10^{2}
739) $HOCH_2CH(CH_3)CH(CH_3)O_2 + NO \rightarrow HOCH_2CH(CH_3)CH(CH_3)ONO_2$	8.2×10^{-13}	-1.8×10^{2}
740) $HOCH_2CH(CH_3)CH(CH_3)(O) + O_2 \rightarrow HOCH_2CH(CH_3)COCH_3 + HO_2$	2.2×10^{-14}	1.2×10^{2}
741) $HOCH_2CH(CH_3)CH(CH_3)(O) \rightarrow HOCH_2CH(CH_3)O_2 + CH_3CHO$	1.0×10^{4}	6.6×10^{3}
742) $n\text{-}C_3H_7CH{=}CH(OH) + HO \rightarrow n\text{-}C_3H_7CH(O_2)CH(OH)_2$	7×10^{-11}	?
743) $n\text{-}C_3H_7CH(O_2)CH(OH)_2 + NO \rightarrow 0.89\,NO_2 + 0.89\ n\text{-}C_3H_7CHO + 0.89\ HCO_2H + 0.89HO_2 + 0.11n\text{-}C_3H_7CH(ONO_2)CH(OH)_2$	7.6×10^{-12}	-1.8×10^{2}
744) $(CH_3)_2CHCH(CH_3)COO_2 + NO \rightarrow NO_2 + CO_2 + (CH_3)_2CHCH(CH_3)O_2$	1.0×10^{-11}	?
745) $HOCH_2CH(CH_3)CH(CH_3)COO_2 + NO \rightarrow HOCH_2CH(CH_3)CH(CH_3)O_2 + CO_2 + NO_2$	1.0×10^{-11}	?
746) $CH_3COC(CH_2O_2){=}C(CH_3)_2 + NO \rightarrow$ 0.77 NO_2 +0.77  $CH_3COC(O_2)C(CH_3)_2$ with CH_2—O + 0.23  $CH_3COC(ONO_2)C(CH_3)_2$ with CH_2—O	7.6×10^{-12}	-1.8×10^{2}

747) 

$CH_3COC(O_2)C(CH_3)_2$ / CH_2—O + NO -->

0.77 NO_2

+ 0.77 $CH_3COCOCH_2OC(CH_3)_2(O_2)$

+ 0.23 $CH_3COCOCH_2OC(CH_3)_2ONO_2$ 7.6×10^{-12} -1.8×10^2

748) $CH_3COCOCH_2OC(CH_3)_2O_2$ + NO -->

0.77 NO_2 +0.77 $CH_3COCOCHO$

+ 0.77 HO_2 + 0.77 CH_3COCH_3 +

0.23 $CH_3COCOCH_2O(CH_3)_2ONO_2$ 7.6×10^{-12} -1.8×10^2

749) CH_2=CH(OH) + O_3 --> 0.2 CH_2OO +

0.2 HC(OH)OO + 0.5 HCO_2H +

0.5 CH_2O + 0.3 HO_2 + 0.39 H_2O

+ 0.27 CO_2 + 0.33 CO + 0.06 H_2 1.1×10^{-17}? 2.1×10^3?

750) HC(OH)OO + NO --> NO_2 + HCO_2H 7×10^{-12} ?

751) HC(OH)OO + SO_2 --> H_2SO_4 +

HCO_2H 7×10^{-12} ?

752) HC(OH)OO + H_2O --> CH_3COO_2H +

H_2O 4×10^{-16} ?

753) CH_3CH=CH(OH) + O_3 -->

0.2 CH_3CHOO + 0.5 HCO_2H + 0.5 CH_3CHO

+ 0.2 HC(OH)OO + 0.36 HO_2 + 0.24 CO_2 +

0.41 CO + 0.06 H_2 + 0.57 H_2O

+ 0.25 CH_3O_2 1.8×10^{-16}? 1.1×10^3?

754) $CH_3C(OH){=}CHCH_3 + O_3$ --> $0.2\ CH_3C(OH)OO + 0.5\ CH_3CHO$ $0.5\ CH_3CO_2H + 0.2\ CH_3CHOO +$ $0.06\ CH_4 + 0.48\ CO_2 + 0.12\ CO$ $+ 0.14\ HO_2 + 0.09\ HO +$ $0.02\ CH_3O + 0.21\ CH_3O_2 +$ $0.3\ H_2O + 0.3\ CH_2O$	1.8×10^{-16}?	1.1×10^{3}?
755) $CH_3C(OH){=}CH_2 + O_3$ --> $0.21\ HO_2 + 0.2\ CH_3C(OH)OO + 0.5\ CH_2O$ $+ 0.24\ CO_2 + 0.5\ CH_3CO_2H + 0.2\ CH_2OO$ $+ 0.15\ CH_3COO_2 + 0.15\ CH_3OH + 0.21\ CO$ $+ 0.06\ H_2 + 0.21\ H_2O$	1.2×10^{-17}	1.67×10^{3}
756) $CH_3C(OH)OO + NO$ --> $NO_2 +$ CH_3CO_2H	7×10^{-12}	?
757) $CH_3C(OH)OO + SO_2$ --> $H_2SO_4 +$ CH_3CO_2H	7×10^{-12}	?
758) $CH_3C(OH)OO + H_2O$ --> CH_3COO_2H $+ H_2O$	4×10^{-16}	?
759) $C_2H_5C(OH){=}CH_2 + O_3$ --> $0.2\ C_2H_5C(OH)OO + 0.5\ CH_2O$ $+ 0.5\ C_2H_5CO_2H + 0.2\ CH_2OO$ $+ 0.36\ HO_2 + 0.24\ CO_2 +$ $0.41\ CO + 0.06\ H_2 +$ $0.57\ H_2O + 0.28\ C_2H_5O_2$	1.2×10^{-17}	1.67×10^{3}

760) $C_2H_5C(OH)OO + SO_2$ --> $C_2H_5CO_2H + H_2SO_4$	7×10^{-12}	?
761) $C_2H_5C(OH)OO + NO$ --> $NO_2 + C_2H_5CO_2H$	7×10^{-12}	?
762) $C_2H_5C(OH)OO + H_2O$ --> $C_2H_5COO_2H + H_2O$	4×10^{-16}	?
763) $n\text{-}C_3H_7CH{=}CH(OH) + O_3$ --> $0.2\ n\text{-}C_3H_7CHOO + 0.5\ HCO_2H + 0.5\ n\text{-}C_3H_7CHO + 0.2\ HC(OH)OO + 0.45\ CO_2 + 0.15\ HO_2 + 0.15\ HO$ $0.15\ n\text{-}C_3H_7O_2 + 0.15\ n\text{-}C_3H_7COO_2$	1.8×10^{-16}?	1.1×10^{3}
764) $n\text{-}C_3H_7CHOO + SO_2$ --> $H_2SO_4 + n\text{-}C_3H_7CHO$	7×10^{-12}	?
765) $n\text{-}C_3H_7CHOO + NO$ --> $NO_2 + n\text{-}C_3H_7CHO$	7×10^{-12}	?
766) $n\text{-}C_3H_7CHOO + H_2O$ --> $n\text{-}C_3H_7CO_2H + H_2O$	4×10^{-16}	
767) $CH_3COO_2NO_2 + HO$ --> $H_2O + O_2CH_2COO_2NO_2$	1.4×10^{-13}	6.5×10^{2}
768) $O_2CH_2COO_2NO_2 + NO$ --> $NO_2 + OCH_2COO_2NO_2$	7.6×10^{-12}	-1.8×10^{2}
769) $OCH_2COO_2NO_2$ (+M) --> $CH_2O + CO_2 + NO_3$	1.1×10^{5}	5.8×10^{3}
770) $OCH_2COO_2NO_2 + O_2$ --> $HO_2 + HCOCOO_2NO_2$	7.4×10^{-15}	6.5×10^{2}

REACTIONS OF THE HYDROPEROXIDES

771) CH_3O_2H + hv --> CH_3O + HO	J(MeO_2H)	-----
772) HO_2CH_2OH + hv --> HCO_2H + HO_2 + HO	J(772)	-----
773) $CH_2(Cl)(O_2H)$ + hv --> HCOCl + HO_2 + HO	J(773)	-----
774) $C_2H_5O_2H$ + hv --> CH_3CHO + HO_2 + HO	J(774)	-----
775) $CH_3CH(OH)O_2H$ + hv --> CH_3CO_2H + HO_2 + HO	J(775)	-----
776) $HOCH_2CH_2O_2H$ + hv --> $HOCH_2CHO$ HO_2 + HO	J(776)	-----
777) $HOCH_2CH(OH)O_2H$ + hv --> HO + $HOCH_2CO_2H$ + HO_2	J(777)	-----
778) CH_2=CHO_2H + hv --> O_2CH_2CHO + HO	J(778)	-----
779) HO_2CH_2CHO + hv --> $(HCO)_2$ + HO_2 + HO	J(779)	-----
780) $HO_2CH_2CH_2ONO_2$ + hv --> HO + HO_2 + O_2NOCH_2CHO	J(780)	-----
781) $HCOCH(O_2H)(ONO_2)$ + hv --> HO + $HCOCO_2NO_2$ + HO_2	J(781)	-----
782) $ClC_2H_4O_2H$ + hv --> HO + $ClCH_2CHO$ + HO_2	J(782)	-----

783) $CH_3CH(Cl)(O_2H)$ + hv --> HO + CH_3COCl + HO_2	J(783)	-----
784) $i\text{-}C_3H_7O_2H$ + hv --> HO + HO_2 + C_2H_5CHO	J(784)	-----
785) $HOCH_2CH_2CH_2O_2H$ + hv --> HO + $HOCH_2CH_2CHO$ + HO_2	J(785)	-----
786) $n\text{-}C_3H_7O_2H$ + hv --> HO + HO_2 + C_2H_5CHO	J(786)	-----
787) $CH_3COCH_2O_2H$ + hv --> HO + HO_2 + CH_3COCHO	J(787)	-----
788) $CH_3C(OH)(O_2H)CH_2OH$ + hv --> HO + CH_3CO_2H + HO_2 + CH_2O	J(788)	-----
789) $HOCH_2C(OH)(O_2H)CH_2OH$ + hv --> HO + $HOCH_2CO_2H$ + HO_2 + CH_2O	J(789)	-----
790) $CH_3CH(O_2)CH_2OH$ + hv --> HO + CH_3COCH_2OH + HO_2	J(790)	-----
791) $CH_3CH(OH)CH_2O_2H$ + hv --> HO + HO_2 + $CH_3CH(OH)CHO$	J(791)	-----
792) $HO_2CH_2COCO_2H$ + hv --> HO + + HO_2 + $HCOCOCO_2H$	J(792)	-----
793) $HCOCH{=}CHO_2H$ + hv --> HO + $HCOCH(O_2)CHO$	J(793)	-----
794) $HCOCH(O_2H)CHO$ + hv --> HO + HO_2 + $(HCO)_2$ + CO	J(794)	-----

795) $CH_2=C(CH_3)(O_2H)$ + hv --> HO + $O_2CH_2COCH_3$	J(795)	-----
796) $CH_3CH(O_2H)CH_2ONO_2$ + hv --> HO HO_2 + $CH_3COCH_2ONO_2$	J(796)	-----
797) $CH_3COCH(O_2H)(ONO_2)$ + hv --> HO + HO_2 + $CH_3COCO_2NO_2$	J(797)	-----
798) $ClC_3H_6O_2H$ + hv --> HO + HO_2 + $ClCH_2COCH_3$	J(798)	-----
799) sec-$C_4H_9O_2H$ + hv --> HO + HO_2 + $CH_3COC_2H_5$	J(799)	-----
800) n-$C_4H_9O_2H$ + hv --> HO + HO_2 + n-C_3H_7CHO	J(800)	-----
801) t-$C_4H_9O_2H$ + hv --> HO + t-C_4H_9O	J(801)	-----
802) i-$C_4H_9O_2H$ + hv --> HO + HO_2 + i-C_3H_7CHO	J(802)	-----
803) $CH_3COCH(O_2)CH_3$ + hv --> HO + HO_2 + $CH_3COCOCH_3$	J(803)	-----
804) $C_2H_5COCH_2O_2H$ + hv --> HO + HO_2 + C_2H_5COCHO	J(804)	-----
805) $HO_2CH_2CH_2CH_2CH_2OH$ + hv --> HO + $OCH_2CH_2CH_2CH_2OH$	J(805)	-----
806) $HOCH_2C(OH)(O_2H)CH(OH)CH_3$ + hv --> HO + $HOCH_2CO_2H$ + $CH_3CH(OH)O_2$	J(806)	-----

807) $CH_3CH(OH)CH(O_2H)CH_3$ + hv --> HO + $CH_3CH(OH)CH(O)CH_3$	J(807)	-----
808) $C_2H_5C(OH)(O_2H)CH_2OH$ + hv --> HO + $C_2H_5CO_2H$ + HO_2 + CH_2O	J(808)	-----
809) $CH_3COCH{=}CHO_2H$ + hv --> HO + + $CH_3COCH(O_2)CHO$	J(809)	-----
810) $CH_3COCH(O_2H)CHO$ + hv --> HO + $CH_3COCOCHO$ + HO_2	J(810)	-----
811) $HOCH_2C(CH_3)(O_2H)CHO$ + hv --> HO + CH_2O + HO_2 + CH_3COCHO	J(811)	-----
812) $O_2NOCH_2C(CH_3)(O_2H)CHO$ + hv --> HO + NO_2 + CH_2O + CH_3COCHO	J(812)	-----
813) $CH_3COCH(O_2H)CH_2OH$ + hv --> HO + HO_2 + $CH_3COCOCH_2OH$	J(813)	-----
814) $HCOCH{=}C(CH_3)O_2H$ + hv --> HO + $CH_3COCH(O_2)CHO$	J(814)	-----
815) $CH_3COCH(O_2H)CH_2ONO_2$ + hv --> HO + HO_2 + $CH_3COCOCH_2ONO_2$	J(815)	-----
816) $CH_3CH(O_2H)CH(ONO_2)CH_3$ + hv --> HO + HO_2 + $CH_3COCH(ONO_2)CH_3$	J(816)	-----
817) $(CH_3)_2C(O_2H)CH_2OH$ + hv --> HO + CH_3COCH_3 + HO_2 + CH_2O	J(817)	-----
818) $(CH_3)_2C(O_2H)CH_2ONO_2$ + hv --> HO + CH_3COCH_3 + NO_2 + CH_2O	J(818)	-----

819) $CH_3CH(Cl)CH(O_2H)CH_3$ + hv -->

HO + $CH_3CH(Cl)COCH_3$ + HO_2 J(819) -----

820) $(CH_3)_2C(O_2H)CH_2Cl$ + hv -->

HO + CH_3COCH_3 + $CH_2(Cl)(O_2)$ J(820) -----

821) $C_5H_{11}O_2H$ + hv --> $C_5H_{11}O$ +

HO J(821) -----

822) $(CH_3)_2CHCH(CH_3)O_2H$ + hv -->

HO + $(CH_3)_2CHCH(CH_3)O$ J(822) -----

823) $HOCH_2CH(CH_3)CH(CH_3)O_2H$ + hv -->

HO + $HOCH_2CH(CH_3)CH(CH_3)O$ J(823) -----

824) $CH_3COCH(OH)CH(O_2H)CHO$ + hv -->

HO + CH_3COCHO + $(HCO)_2$ + HO_2 J(824) -----

825) $C_5H_{10}(OH)O_2H$ + hv --> HO +

$HOC_4H_9(C{=}O)$ + HO_2 J(825) -----

826) $HCOCH(OH)C(O_2H)(CH_3)CHO$ + hv -->

HO + HO_2 + CH_3COCHO + $(HCO)_2$ J(826) -----

827) $HOCH_2C(CH_3)(O_2H)CH{=}CH_2$ + hv -->

HO + HO_2 + CH_2O + $CH_3COCH{=}CH_2$ J(827) -----

828) $CH_2{=}CH(CH_3)CH(O_2H)CH_2OH$ + hv -->

HO + CH_2O + HO_2 + $CH_2{=}C(CH_3)CHO$ J(828) -----

829) $HO_2CH_2CH(CH_3)CH(CH_3)OH$ + hv -->

HO + $OCH_2CH(CH_3)CH(CH_3)OH$ J(829) -----

830) $O_2NOCH_2C(CH_3)(O_2H)CH{=}CH_2$ + hv -->

HO + CH_2O + $CH_3COCH{=}CH_2$ + NO_2 J(830) -----

831) $CH_2{=}CH(CH_3)CH(O_2H)CH_2ONO_2$ + hv -->

$HO + NO_2 + CH_2O + CH_2{=}C(CH_3)CHO$ J(831) -----

832) $C_6H_{13}O_2H$ + hv --> $HO + C_6H_{13}O$ J(832) -----

833) $(CH_3)_2CHC(O_2H)(CH_3)_2$ + hv -->

$HO + CH_3COCH_3 + i\text{-}C_3H_7O_2$ J(833) -----

834) $(CH_3)_2CHCH(CH_3)CH_2O_2H$ + hv -->

$HO + HO_2 + (CH_3)_2CHCH(CH_3)CHO$ J(834) -----

835) $HOCH_2CH(CH_3)CH(CH_2O_2H)CH_2OH$ +

hv --> HO +

$HOCH_2CH(CH_3)CH(CH_2O)CH_2OH$ J(835) -----

836) $HOCH_2CH(CH_2O_2H)CH(CH_2OH)_2$ + hv

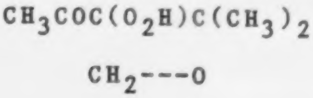
--> $HO + HO_2$ +

$(HOCH_2)_2CHCH(CH_2OH)CHO$ J(836) -----

837) $C_6H_{12}(OH)O_2H$ + hv --> $HO + HO_2$

$+ HOC_5H_{11}(C{=}O)$ J(837) -----

838) $C_6H_5O_2H$ + hv --> $HO + C_6H_5O$ J(838) -----

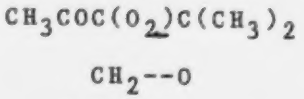
839) 
$\underset{CH_2{-}{-}{-}O}{CH_3COC(O_2H)C(CH_3)_2}$ + hv -->

$HO + CH_3COCOCH_2OC(CH_3)_2O_2$ J(839) -----

840) $CH_3COCOCH_2OC(CH_3)_2O_2H$ + hv -->

$HO + CH_3COCOCHO + HO_2 + CH_3COCH_3$ J(840) -----

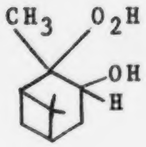
841) $CH_3COC(CH_2O_2H){=}C(CH_3)_2$ + hv -->

HO + 
$\underset{CH_2{-}{-}O}{CH_3COC(O_2)C(CH_3)_2}$ J(841) -----

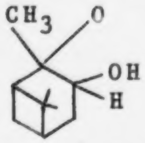
842) $C_7H_{15}O_2H$ + hv --> $HO + C_7H_{15}O$ J(842) -----

843) $C_6H_5CH_2O_2H$ + hv --> HO + $C_6H_5CH_2O$	J(843)	-----
844) $C_7H_{14}(OH)O_2H$ + hv --> HO + HO_2 + $HOC_6H_{13}(C{=}O)$	J(844)	-----
845) $C_8H_{17}O_2H$ + hv --> HO + $C_8H_{17}O$	J(845)	-----
846) $C_8H_{16}(OH)O_2H$ + hv --> HO + HO_2 + $HOC_7H_{15}(C{=}O)$	J(846)	-----
847) R_1O_2H + hv --> HO + R_1O	J(847)	-----
848) R_2O_2H + hv --> HO + R_2O	J(848)	-----
849) YO_2H + hv --> HO + YO	J(849)	-----
850) CH_3COO_2H + hv --> HO + CH_3O_2 + CO_2	J(850)	-----
851) $HCOCOO_2H$ + hv --> HO + HO_2 + CO_2 + CO	J(851)	-----
852) $C_2H_5COO_2H$ + hv --> HO + CO_2 + $C_2H_5O_2$	J(852)	-----
853) CH_3COCOO_2H + hv --> HO + CO_2 + CH_3COO_2	J(853)	-----
854) $HCOCH(ONO_2)COO_2H$ + hv --> HO $HCOCH(O_2)(ONO_2)$	J(854)	-----
855) i-$C_3H_7COO_2H$ + hv --> HO + i-$C_3H_7O_2$ + CO_2	J(855)	-----
856) n-$C_3H_7COO_2H$ + hv --> HO + n-$C_3H_7O_2$ + CO_2	J(856)	-----

857) $(CH_3)_2C(OH)COO_2H + hv \rightarrow HO + HO_2 + CO_2 + CH_3COCH_3$	J(857)	-----
858) $HCOCH{=}CHCOO_2H + hv \rightarrow HO + CO_2 + HCOCH{=}CHO_2$	J(858)	-----
859) $CH_3COCH(ONO_2)COO_2H + hv \rightarrow HO + CO_2 + CH_3COCH(O_2)(ONO_2)$	J(859)	-----
860) $sec\text{-}C_4H_9COO_2H + hv \rightarrow HO + sec\text{-}C_4H_9O_2 + CO_2$	J(860)	-----
861) $n\text{-}C_4H_9COO_2H + hv \rightarrow HO + n\text{-}C_4H_9O_2 + CO_2$	J(861)	-----
862) $i\text{-}C_4H_9COO_2H + hv \rightarrow HO + i\text{-}C_4H_9O_2 + CO_2$	J(862)	-----
863) $CH_3COCH{=}CHCOO_2H + hv \rightarrow HO\ CO_2 + CH_3COCH{=}CHO_2$	J(863)	-----
864) $HCOCH{=}C(CH_3)COO_2H + hv \rightarrow HO + HCOCH{=}C(CH_3)O_2 + CO_2$	J(864)	-----
865) $C_6H_5COO_2H + hv \rightarrow HO + CO_2 + C_6H_5O_2$	J(865)	-----
866) $R_1COO_2H + hv \rightarrow HO + CO_2 + R_1O_2$	J(866)	-----
867) $R_2COO_2H + hv \rightarrow HO + CO_2 + R_2O_2$	J(867)	-----

868) 

+ hv --> HO +



J(868) -----

869) CH_3O_2H + HO --> 0.5 CH_3O_2 + H_2O
0.5 CH_2O + 0.5 HO 1×10^{-11} ?

870) HO_2CH_2OH + HO --> H_2O +
0.5 O_2CH_2OH + 0.5 HCO_2H + 0.5 OH 1×10^{-11} ?

871) $CH_2(Cl)(O_2H)$ + HO --> H_2O + 0.5 HO
+ 0.5 HC(Cl)O + 0.5 $CH_2(Cl)(O_2)$ 1×10^{-11} ?

872) $C_2H_5O_2H$ + HO --> H_2O + 0.5 $C_2H_5O_2$
0.5 CH_3CHO + 0.5 HO 1×10^{-11} ?

873) $CH_3CH(OH)O_2H$ + HO --> H_2O +
0.5 $CH_3CH(OH)O_2$ + 0.5 HO +
0.5 CH_3CO_2H 1×10^{-11} ?

874) $HOCH_2CH_2O_2H$ + HO --> H_2O +
0.5 $HOCH_2CH_2O_2$ + 0.5 HO +
0.5 $HOCH_2CHO$ 1×10^{-11} ?

875) $HOCH_2CH(OH)O_2H$ + HO --> H_2O +
+ 0.5 HO + o.5 $HOCH_2CO_2H$ +
0.5 $HOCH_2CH(OH)O_2$ 1×10^{-11} ?

876) $CH_2{=}CHO_2H$ + HO --> H_2O +
$HOCH_2CH(O_2)O_2H$ 1×10^{-11} ?

877) $HOCH_2CH(O_2)O_2H$ + NO --> NO_2 + $HOCH_2COO_2H$ + HO_2	7.6×10^{-12}	?
878) HO_2CH_2CHO + HO --> H_2O + $HO_2CH_2COO_2$	1.2×10^{-11}	?
879) $HO_2CH_2COO_2$ + NO --> NO_2 + HO + CH_2O + CO_2	7.6×10^{-12}	?
880) $HO_2CH_2CH_2ONO_2$ + HO --> H_2O + 0.5 HO + 0.5 O_2NOCH_2CHO + 0.5 $O_2CH_2CH_2ONO_2$	1×10^{-11}	?
881) $HCOCH(O_2H)(ONO_2)$ + HO --> H_2O $O_2NOCH(O_2H)COO_2$	1.2×10^{-11}	?
882) $O_2NOCH(O_2H)COO_2$ + NO --> NO_2 + CO_2 + $O_2NOCH(O_2H)(O_2)$	7.6×10^{-12}	?
883) $O_2NOCH(O_2H)(O_2)$ + NO --> NO_2 + HONO + HO + CO_2 + O_2	7.6×10^{-12}	?
884) $ClC_2H_4O_2H$ + HO --> H_2O + 0.5 HO + 0.5 $ClCH_2CHO$ + 0.5 $ClC_2H_4O_2$	1×10^{-11}	?
885) $CH_3CH(Cl)(O_2H)$ + HO --> H_2O + 0.5 HO + 0.5 CH_3COCl + 0.5 $CH_3CH(Cl)(O_2)$	1×10^{-11}	?
886) i-$C_3H_7O_2H$ + HO --> H_2O + 0.5 HO + 0.5 CH_3COCH_3 + 0.5 $C_3H_7O_2$	1×10^{-11}	?

887) $HOCH_2CH_2CH_2O_2H$ + HO --> H_2O +
0.5 HO + 0.5 $HOCH_2CH_2CHO$ +
0.5 $HOCH_2CH_2CH_2O_2$ 1×10^{-11} ?

888) $n\text{-}C_3H_7O_2H$ + HO --> H_2O +
0.5 HO + 0.5 C_2H_5CHO
+ 0.5 $n\text{-}C_3H_7O_2$ 1×10^{-11} ?

889) $CH_3COCH_2O_2H$ + HO --> H_2O +
0.5 HO + 0.5 CH_3COCHO
+ 0.5 $CH_3COCH_2O_2$ 1×10^{-11} ?

890) $CH_3C(OH)(O_2H)CH_2OH$ + HO --> H_2O
0.5 HO + CH_3COO_2H + 0.5 CH_2O
+ 0.5 HO_2 + 0.5 $CH_3C(OH)(O_2)CH_2OH$ 1×10^{-11} ?

891) $HOCH_2C(OH)(O_2H)CH_2OH$ + HO -->
H_2O + 0.5 $HOCH_2C(OH)(O_2)CH_2OH$
+ 0.5 HO + 0.5 $HOCH_2COO_2H$
+ 0.5 CH_2O + 0.5 HO_2 1×10^{-11} ?

892) $CH_3CH(O_2H)CH_2OH$ + HO --> H_2O +
0.5 HO + 0.5 CH_3COCH_2OH
+ 0.5 $CH_3CH(O_2)CH_2OH$ 1×10^{-11} ?

893) $CH_3CH(OH)CH_2O_2H$ + HO --> H_2O +
0.5 HO + 0.5 $CH_3CH(OH)CHO$
+ 0.5 $CH_3CH(OH)CH_2O_2$ 1×10^{-11} ?

894) $HO_2CH_2COCO_2H$ + HO --> H_2O +
0.5 HO + 0.5 $HCOCOCO_2H$
+ 0.5 $O_2CH_2COCO_2H$ 1×10^{-11} ?

895) $HCOCH{=}CHO_2H$ + HO --> $HO_2CH(O_2)CH(OH)(CHO)$	1×10^{-11}	?
896) $HO_2CH(O_2)CH(OH)(CHO)$ + NO --> $NO_2 + HCOO_2H + (HCO)_2 + HO_2$	7.6×10^{-12}	?
897) $HCOCH(O_2H)CHO$ + HO --> H_2O + 0.5 HO + 0.5 HCOCOCHO + 0.5 $HCOCH(O_2)CHO$	1×10^{-11}	?
898) $CH_2{=}C(CH_3)(O_2H)$ + HO --> $HOCH_2C(CH_3)(O_2)(O_2H)$	1×10^{-11}	?
899) $HOCH_2C(CH_3)(O_2)(O_2H)$ + NO --> $NO_2 + CH_3COO_2H + CH_2O + HO_2$	7.6×10^{-12}	?
900) $CH_3CH(O_2H)CH_2ONO_2$ + HO --> H_2O 0.5 HO + 0.5 $CH_3COCH_2ONO_2$ + 0.5 $CH_3CH(O_2)CH_2ONO_2$	1×10^{-11}	?
901) $CH_3COCH(O_2H)(ONO_2)$ + HO --> H_2O 0.5 HO + 0.5 $CH_3COCO_2NO_2$ + 0.5 $CH_3COCH(O_2)(ONO_2)$	1×10^{-11}	?
902) $ClC_3H_6O_2H$ + HO --> H_2O + 0.5 HO + $ClCH_2COCH_3$ + 0.5 $ClC_3H_6O_2$	1×10^{-11}	?
903) sec-$C_4H_9O_2H$ + HO --> H_2O + 0.5 HO + 0.5 $CH_3COC_2H_5$ + 0.5 sec-$C_4H_9O_2$	1×10^{-11}	?

904) n-$C_4H_9O_2H$ + HO --> H_2O +

0.5 HO + 0.5 n-C_3H_7CHO +

0.5 n-$C_4H_9O_2$ 1×10^{-11} ?

905) t-$C_4H_9O_2H$ + HO --> H_2O +

t-$C_4H_9O_2$ 3×10^{-12} ?

906) i-$C_4H_9O_2H$ + HO --> H_2O +

0.5 HO + 0.5 i-C_4H_9CHO +

0.5 i-$C_4H_9O_2$ 1×10^{-11} ?

907) $CH_3COCH(O_2H)CH_3$ + HO --> H_2O +

0.5 HO + 0.5 $CH_3COCOCH_3$ +

0.5 $CH_3COCH(O_2)CH_3$ 1×10^{-11} ?

908) $C_2H_5COCH_2O_2H$ + HO --> H_2O +

0.5 HO + 0.5 C_2H_5COCHO +

0.5 $C_2H_5COCH_2O_2$ 1×10^{-11} ?

909) $HO_2CH_2CH_2CH_2CH_2OH$ + HO --> H_2O

+ 0.5 HO + 0.5 $HOCH_2CH_2CH_2CHO$

+ 0.5 $O_2CH_2CH_2CH_2CH_2OH$ 1×10^{-11} ?

910) $HOCH_2C(OH)(O_2H)CH(OH)CH_3$ + HO -->

H_2O + 0.5 $HOCH_2C(OH)(O_2)CH(OH)CH_3)$

+ 0.5 HO + 0.5 $HOCH_2COO_2H$ 1×10^{-11} ?

911) $CH_3CH(OH)CH(O_2H)CH_3$ + HO -->

H_2O + 0.5 $CH_3CH(OH)CH(O_2)CH_3$

+ 0.5 HO + 0.5 $CH_3COCH(OH)CH_3$ 1×10^{-11} ?

912) $C_2H_5C(OH)(O_2H)CH_2OH$ + HO --> H_2O + 0.5 $C_2H_5C(OH)(O_2)CH_2OH$ + 0.5 HO + 0.5 $C_2H_5COO_2H$ + 0.5 CH_2O + 0.5 HO_2	1×10^{-11}	?
913) $CH_3COCH{=}CHO_2H$ + HO --> $CH_3COCH(O_2)CH(OH)(O_2H)$	1×10^{-11}	?
914) $CH_3COCH(O_2)CH(OH)(O_2H)$ + NO --> NO_2 + CH_3COCHO + $HCOO_2H$ + HO_2	7.6×10^{-12}	?
915) $CH_3COCH(O_2H)CHO$ + HO --> H_2O 0.5 HO + $CH_3COCOCHO$ + 0.5 $CH_3COCH(O_2)CHO$	1×10^{-11}	?
916) $HOCH_2C(CH_3)(O_2H)CHO$ + HO --> H_2O + $HOCH_2C(CH_3)(O_2)CHO$	1×10^{-11}	?
917) $O_2NOCH_2C(CH_3)(O_2H)CHO$ + HO --> H_2O + $O_2NOCH_2C(CH_3)(O_2)CHO$	1×10^{-11}	?
918) $CH_3COCH(O_2H)CH_2OH$ + HO --> H_2O + 0.5 HO + 0.5 $CH_3COCOCH_2OH$ + 0.5 $CH_3COCH(O_2)CH_2OH$	1×10^{-11}	?
919) $HCOCH{=}C(CH_3)O_2H$ + HO --> H_2O + $HCOCH(OH)C(CH_3)(O_2H)(O_2)$	1×10^{-11}	?
920) $HCOCH(OH)C(CH_3)(O_2H)(O_2)$ + NO --> NO_2 + CH_3COO_2H + HO_2 + $(HCO)_2$	7.6×10^{-12}	?
921) $CH_3COCH(O_2H)CH_2ONO_2$ + HO --> H_2O + 0.5 HO + 0.5 $CH_3COCOCH_2ONO_2$ + 0.5 $CH_3COCH(O_2)CH_2ONO_2$	1×10^{-11}	?

922) $CH_3CH(O_2H)CH(ONO_2)CH_3$ + HO --> H_2O + 0.5 HO + 0.5 $CH_3COCH(ONO_2)CH_3$ + 0.5 $CH_3CH(O_2)CH(ONO_2)CH_3$	1×10^{-11}	?
923) $(CH_3)_2C(O_2H)CH_2OH$ + HO --> H_2O $(CH_3)_2C(O_2)CH_2OH$	1×10^{-11}	?
924) $(CH_3)_2C(O_2H)CH_2ONO_2$ + HO --> H_2O + $(CH_3)_2C(O_2)CH_2ONO_2$	1×10^{-11}	?
925) $CH_3CH(Cl)CH(O_2H)CH_3$ + HO --> H_2O + 0.5 HO + 0.5 $CH_3CH(Cl)COCH_3$ + 0.5 $CH_3CH(Cl)CH(O_2)CH_3$	1×10^{-11}	?
926) $(CH_3)_2C(O_2H)CH_2Cl$ + HO --> H_2O + $(CH_3)_2C(O_2)CH_2Cl$	1×10^{-11}	?
927) $C_5H_{11}O_2H$ + HO --> H_2O+ 0.5 HO + 0.5 n-$C_3H_7COCH_3$ + 0.5 $C_5H_{11}O_2$	1×10^{-11}	?
928) $(CH_3)_2CHCH(CH_3)O_2H$ + HO --> H_2O + 0.5 HO + i-$C_3H_7COCH_3$ + 0.5 $(CH_3)_2CHCH(CH_3)O_2$	1×10^{-11}	?
929) $HOCH_2CH(CH_3)CH(CH_3)O_2H$ + HO --> H_2O + 0.5 + 0.5 HO + 0.5 $HOCH_2CH(CH_3)COCH_3$ + 0.5 $HOCH_2CH(CH_3)CH(CH_3)O_2$	1×10^{-11}	?
930) $CH_3COCH(OH)CH(O_2H)CHO$ + HO --> H_2O + 0.5 + 0.5 HO + 0.5 $CH_3COCH(OH)COCHO$ + 0.5 $CH_3COCH(OH)CH(O_2)CHO$	1×10^{-11}	?

931) $C_5H_{10}(OH)O_2H$ + HO --> H_2O +

0.5 + 0.5 HO +

0.5 $CH_3COCH_2CH_2CH_2OH$

+ 0.5 $C_5H_{10}(HO)O_2$ 1 x 10^{-11} ?

932) $HCOCH(OH)C(O_2H)(CH_3)CHO$ + HO -->

H_2O + $HCOCH(OH)C(O_2)(CH_3)CHO$ 1 x 10^{-11} ?

933) $HOCH_2C(CH_3)(O_2H)CH=CH_2$ + HO -->

$HOCH_2C(CH_3)(O_2H)CH(O_2)CH_2OH$ 1 x 10^{-11} ?

934) $HOCH_2C(CH_3)(O_2H)CH(O_2)CH_2OH$ + NO

--> NO_2 + $HOCH_2C(CH_3)(O_2H)COCH_2OH$

+ HO_2 7.6 x 10^{-12} ?

935) $CH_2=C(CH_3)CH(O_2H)CH_2OH$ + HO -->

$HOCH_2CH(O_2)(CH_3)CH(O_2H)CH_2OH$ 1 x 10^{-11} ?

936) $HOCH_2CH(O_2)(CH_3)CH(O_2H)CH_2OH$ +

NO --> NO_2 + CH_3COCH_2OH + HO +

$HOCH_2CHO$ 7.6 x 10^{-11} ?

937) $HO_2CH_2CH(CH_3)CH(CH_3)OH$ + HO -->

H_2O + 0.5 $O_2CH_2CH(CH_3)CH(CH_3)OH$

+ 0.5 HO + 0.5 $CH_3CH(OH)CH(CH_3)CHO$ 1 x 10^{-11} ?

938) $O_2NOCH_2C(CH_3)(O_2H)CH=CH_2$ + HO -->

$O_2NOCH_2C(CH_3)(O_2H)CH(O_2)CH_2OH$ 1 x 10^{-11} ?

939) $O_2NOCH_2C(CH_3)(O_2H)CH(O_2)CH_2OH$ +

NO --> NO_2 + $HOCH_2CHO$

+ $CH_3COCH_2ONO_2$ + HO 7.6 x 10^{-12} ?

940) $CH_2{=}CH(CH_3)CH(O_2H)CH_2ONO_2$ + HO

--> $HOCH_2CH(O_2)(CH_3)CH(O_2H)CH_2ONO_2$ 1×10^{-11} ?

941) $HOCH_2CH(O_2)(CH_3)CH(O_2H)CH_2ONO_2$

+ NO --> NO_2 + CH_3COCH_2OH

+ HO + O_2NOCH_2CHO 7.6×10^{-12} ?

942) $C_6H_{13}O_2H$ + HO --> H_2O +

0.5 HO + 0.5 $i\text{-}C_3H_7O_2$

+ 0.5 CH_3COCH_3 + 0.5 $C_6H_{13}O_2$ 1×10^{-11} ?

943) $(CH_3)_2CHC(O_2H)(CH_3)_2$ + HO -->

H_2O + $(CH_3)_2CHC(O_2)(CH_3)_2$ 1×10^{-11} ?

944) $(CH_3)_2CHCH(CH_3)CH_2O_2H$ + HO -->

H_2O + 0.5 $(CH_3)_2CHCH(CH_3)CH_2O_2$

+ 0.5 HO + 0.5 $(CH_3)_2CHCH(CH_3)CHO$ 1×10^{-11} ?

945) $HOCH_2CH(CH_3)CH(CH_2O_2H)CH_2OH$ +

HO --> H_2O + 0.5 HO +

0.5 $HOCH_2CH(CH_3)CH(CH_2O_2)CH_2OH$ +

0.5 $HOCH_2CH(CH_3)CH(CH_2OH)CHO$ 1×10^{-11} ?

946) $HOCH_2CH(CH_2O_2H)CH(CH_2OH)_2$ + HO -->

H_2O + 0.5 $HOCH_2CH(CH_2O_2)CH(CH_2OH)_2$

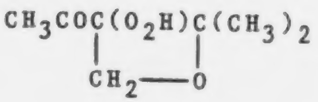
0.5 HO + 0.5 $(HOCH_2)CHCH(CH_2OH)CHO$ 1×10^{-11} ?

947) $C_6H_{12}(OH)O_2H$ + HO --> H_2O +

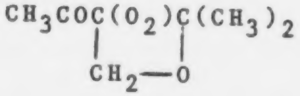
0.5 HO + $C_2H_5COCH_2CH_2CH_2OH$

+ 0.5 $C_6H_{12}(OH)O_2$ 1×10^{-11} ?

948) $C_6H_5O_2H$ + HO --> H_2O + $C_6H_5O_2$ 1×10^{-11} ?

949) 

$CH_3COC(O_2H)C(CH_3)_2$ (ring: CH_2—O) + HO -->

H_2O + 

$CH_3COC(O_2)C(CH_3)_2$ (ring: CH_2—O) 1×10^{-11} ?

950) $CH_3CO(CH_2O_2H)=C(CH_3)_2$ + HO -->

$CH_3CO(CH_2O_2H)(O_2)C(OH)(CH_3)_2$ 1×10^{-11} ?

951) $CH_3CO(CH_2O_2H)(O_2)C(OH)(CH_3)_2$ +

NO --> NO_2 + $CH_3CO_2CH_2OH$ +

CH_3COCH_3 + HO_2 7.6×10^{-12} ?

952) $C_7H_{15}O_2H$ + HO --> H_2O +

0.5 HO + 0.5 CH_3COCH_3 +

0.5 i-$C_4H_9O_2$ + 0.5 $C_7H_{15}O_2$ 1×10^{-11} ?

953) $C_6H_5CH_2O_2H$ + HO --> H_2O +

+ 0.5 HO + 0.5 C_6H_5CHO

+ 0.5 $C_6H_5CH_2O_2$ 1×10^{-11} ?

954) $C_7H_{14}(OH)O_2H$ + HO --> H_2O +

0.5 HO + 0.5 CH_3COCH_3 +

0.5$CH_3CH(O_2)CH_2CH_2OH$

+ 0.5 $C_7H_{14}(OH)O_2$ 1×10^{-11} ?

955) $CH_3CH(O_2)CH_2CH_2OH$ + NO -->

NO_2 + $CH_3COCH_2CH_2OH$ + HO_2 7.6×10^{-12} ?

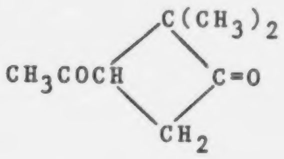
956) $C_8H_{17}O_2H$ + HO --> H_2O +

0.5 HO + 0.5 $C_7H_{16}(C=O)$

+ 0.5 $C_8H_{17}O_2$ 1×10^{-11} ?

957) $C_8H_{16}(OH)O_2H$ + HO --> H_2O +
0.5 HO + 0.5 $HOC_7H_{15}(C=O)$
+ 0.5 $C_8H_{16}(OH)O_2$ 1×10^{-11} ?

958) R_1O_2H + HO --> 0.5 R_1O_2
0.5 HO + 0.5 R_2CHO + H_2O 1×10^{-11} ?

959) R_2O_2H + HO --> 0.5 R_2O_2
0.5 HO + H_2O
+ 0.5  1×10^{-11} ?

960) YO_2H + HO --> YO_2 + H_2O 1×10^{-11} ?

961) CH_3COO_2H + HO --> CH_3COO_2
+ H_2O 1×10^{-11} ?

962) $HCOCOO_2H$ + HO --> $HCOCOO_2$
+ H_2O 1×10^{-11} ?

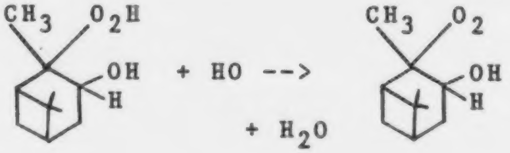
963) $C_2H_5COO_2H$ + HO --> $C_2H_5COO_2$ +
H_2O 1×10^{-11} ?

964) $CH_3COCOCH_2OC(CH_3)_2O_2H$ + HO -->
H_2O + $CH_3COCOCH_2O(CH_3)_2O_2$ 1×10^{-11} ?

965) CH_3COCOO_2H + HO --> H_2O +
CH_3COCOO_2 1×10^{-11} ?

966) $HCOCH(ONO_2)COO_2H$ + HO --> H_2O
+ $HCOCH(ONO_2)COO_2$ 1×10^{-11} ?

967) i-$C_3H_7COO_2H$ + HO --> H_2O +
i-$C_3H_7COO_2$ 1×10^{-11} ?

968) n-$C_3H_7COO_2H$ + HO --> H_2O + n-$C_3H_7COO_2$	1×10^{-11}	?
969) $(CH_3)_2C(OH)COO_2H$ + HO --> H_2O + $(CH_3)_2C(OH)COO_2$	1×10^{-11}	?
970) $HCOCH{=}CHCOO_2H$ + HO --> H_2O + $HCOCH{=}CHCOO_2$	1×10^{-11}	?
971) $CH_3COCH(ONO_2)COO_2H$ + HO --> H_2O + $CH_3COCH(ONO_2)COO_2$	1×10^{-11}	?
972) sec-$C_4H_9COO_2H$ + HO --> H_2O + sec-$C_4H_9COO_2$	1×10^{-11}	?
973) n-$C_4H_9COO_2H$ + HO --> H_2O + n-$C_4H_9COO_2$	1×10^{-11}	?
974) i-$C_4H_9COO_2H$ + HO --> H_2O + i-$C_4H_9COO_2$	1×10^{-11}	?
975) $CH_3COCH{=}CHCOO_2H$ + HO --> H_2O + $CH_3COCH{=}CHCHOO_2$	1×10^{-11}	?
976) $HCOCH{=}C(CH_3)COO_2H$ + HO --> H_2O + $HCOCH{=}C(CH_3)COO_2$	1×10^{-11}	?
977) $C_6H_5COO_2H$ + HO --> H_2O + $C_6H_5COO_2$	1×10^{-11}	?
978) R_1COO_2H + HO --> H_2O + R_1COO_2	1×10^{-11}	?
979) R_2COO_2H + HO --> H_2O + R_2COO_2	1×10^{-11}	?
980)  CH_3 O_2H OH H + HO --> + H_2O CH_3 O_2 OH H	1×10^{-11}	

AMINE CHEMISTRY

981) CH_3NH_2 + HO --> 0.4 CH_3NH + 0.6 $CH_2(O_2)NH_2$ + H_2O	2.2×10^{-11}	-2.3×10^{2}
982) $C_2H_5NH_2$ + HO --> 0.5 C_2H_5NH + 0.5 $CH_3CH(O_2)NH_2$ + H_2O	2.8×10^{-11}	-1.9×10^{2}
983) $(CH_3)_2NH$ + HO --> 0.37 $(CH_3)_2N$ + 0.63 $CH_3(CH_2O_2)NH$ + H_2O	6.5×10^{-11}	-2.5×10^{2}
984) $(CH_3)_3N$ + HO --> $O_2CH_2(CH_3)_2N$ + H_2O	6.1×10^{-11}	-2.5×10^{2}
985) CH_3NH + O_2 --> CH_2=NH + HO_2	6×10^{-18}?	?
986) CH_2=NH + O_3 --> 0.5 CH_2O + [0.5 HNO --> 0.5 NO + 0.5HO_2] + 0.2 CH_2OO + 0.09 CO_2 + 0.21 CO + 0.06 H_2 + 0.21 H_2O [+ HNOO --> HO + NO] + NO + 0.56 HO_2 + 0.5 HO	1.8×10^{-18}?	2.6×10^{3}?
987) CH_2=NH + HO (+M) --> $HOCH_2NHO_2$	8×10^{-12}?	-8.4×10^{0}?
988) $HOCH_2NHO_2$ + NO --> NO_2 + $HOCH_2NHO$	7.6×10^{-12}?	-1.8×10^{2}?
989) $CH_2(O_2)NH_2$ + NO --> CH_2O + NH_2 + NO_2	7.6×10^{-12}	-1.8×10^{2}
990) $HOCH_2NHO$ --> CH_2O + NO + 2HO_2	2.3×10^{-2}?	?
991) $HOCH_2NHO$ + O_2 --> HO_2 + $HOCH_2N$=O	7×10^{-15}?	?

992) $HOCH_2N{=}O + hv \dashrightarrow CH_2O + HO_2 + NO$	J(981)	?
993) $CH_3NH + NO \dashrightarrow CH_3NHN{=}O$	3.9×10^{-12}?	0?
994) $CH_3NHN{=}O + hv \dashrightarrow CH_3NH + NO$	J(MeNHN=O)	-----
995) $CH_3NH + NO_2 \dashrightarrow CH_3NHNO_2$	1.5×10^{-11}?	0?
996) $CH_3NH + O_3 \dashrightarrow CH_3NHO + O_2$	3×10^{-13}?	1.2×10^{3}?
997) $CH_3NHO + O_2 \dashrightarrow CH_3N{=}O + HO_2$	7.4×10^{-15}?	6.5×10^{2}?
998) $CH_3N{=}O + hv \dashrightarrow CH_3O_2 + NO$	J(MeN=O)	-----
999) $C_2H_5NH + NO \dashrightarrow C_2H_5NHN{=}O$	3.9×10^{-12}?	0?
1000) $C_2H_5NHN{=}O + hv \dashrightarrow C_2H_5NH + NO$	J(EtNHN=O)	-----
1001) $C_2H_5NH + NO_2 \dashrightarrow C_2H_5NHNO_2$	1.5×10^{-11}?	0?
1002) $C_2H_5NH + O_3 \dashrightarrow C_2H_5NHO + O_2$	3×10^{-13}?	1.2×10^{3}?
1003) $C_2H_5NHO + O_2 \dashrightarrow C_2H_5N{=}O + HO_2$	7×10^{-15}?	6.5×10^{2}?
1004) $C_2H_5N{=}O + hv \dashrightarrow C_2H_5O_2 + NO$	J(EtN=O)	-----
1005) $(CH_3)_2N + NO \dashrightarrow (CH_3)_2NN{=}O$	3.9×10^{-12}?	0?
1006) $(CH_3)_2NN{=}O + hv \dashrightarrow (CH_3)_2N + NO$	J($Me_2NN{=}O$)	-----
1007) $CH_3CH(O_2)NH_2 + NO \dashrightarrow CH_3CHO + NH_2 + NO_2$	7.6×10^{-12}?	-1.8×10^{2}?
1008) $CH_3(CH_2O_2)NH + NO \dashrightarrow CH_2O + CH_3NH + NO_2$	7.6×10^{-12}?	-1.8×10^{2}?
1009) $(CH_3)_2N + NO_2 \dashrightarrow (CH_3)_2NNO_2$	1.5×10^{-11}?	0?
1010) $(CH_3)_2N + NO_2 \dashrightarrow HONO + CH_2{=}NCH_3$	3.3×10^{-12}?	?

1011) $(CH_3)_2N + O_2$ --> $CH_2{=}NCH_3 + HO_2$	5.9×10^{-18}?	?
1012) $(CH_3)_2N + O_3$ --> $(CH_3)_2NO + O_2$	3×10^{-13}?	1.2×10^{3}?
1013) $(CH_3)_2NO$ --> $CH_3O_2 + CH_3N{=}O$	1.4×10^{-14}?	2.3×10^{2}?
1014) $CH_2{=}NCH_3 + O_3$ --> $CH_2OO + CH_3N{=}O$	1×10^{-17}?	2×10^{3}?
1015) $CH_2{=}NCH_3 + HO$ --> $HOCH_2N(O_2)CH_3$	3×10^{-11}?	-1.3×10^{1}?
1016) $HOCH_2N(O_2)CH_3 + NO$ --> $HO_2 + CH_2O + CH_3NO + NO_2$	7.6×10^{-12}?	-1.8×10^{2}?
1017) $O_2CH_2N(CH_3)_2 + NO$ --> $NO_2 + CH_2O + (CH_3)_2N$	7.6×10^{-12}	-1.8×10^{2}?

CHLORINE CHEMISTRY

1018) $Cl_2 + hv \rightarrow 2Cl$	$J(Cl_2)$	-----
1019) $Cl + CH_4 \rightarrow HCl + CH_3O_2$	1.0×10^{-13}	1.35×10^3
1020) $Cl + NO_2\ (+M) \rightarrow ClNO_2$	1.0×10^{-10}	?
1021) $Cl + NO\ (+M) \rightarrow ClNO$	5×10^{-11}	?
1022) $ClNO + hv \rightarrow Cl + NO$	$J(ClNO)$	-----
1023) $Cl + HO_2 \rightarrow HCl + O_2$	3.2×10^{-11}	?
1024) $Cl + O_3 \rightarrow ClO + O_2$	1.13×10^{-11}	?
1025) $ClO + NO \rightarrow Cl + NO_2$	1.75×10^{-11}	?
1026) $ClO + NO_2\ (+M) \rightarrow ClONO_2$	2.8×10^{-12}	?
1027) $ClONO_2 + hv \rightarrow Cl + NO_3$	$J(ClONO_2)$	-----
1028) $ClO + HO_2 \rightarrow HOCl + O_2$	3.8×10^{-12}	?
1029) $HOCl + hv \rightarrow HO + Cl$	$J(HOCl)$	-----
1030) $Cl + C_2H_6 \rightarrow HCl + C_2H_5O_2$	6.4×10^{-11}	0
1031) $Cl + C_3H_8 \rightarrow HCl +$ $0.3\ n\text{-}C_3H_7O_2$ $+ 0.7\ i\text{-}C_3H_7O_2$	1.3×10^{-10}	0
1032) $Cl + n\text{-}C_4H_{10} \rightarrow HCl +$ $0.x\ sec\text{-}C_4H_9O_2 + 0.y\ n\text{-}C_4H_9O_2$	2.0×10^{-10}	0
1033) $Cl + iso\text{-}C_4H_{10} \rightarrow HCl +$ $0.x\ t\text{-}C_4H_9O_2 + 0.y\ iso\text{-}C_4H_9O_2$	1.4×10^{-10}	0
1034) $(CH_3)_2CHCH(CH_3)_2 + Cl \rightarrow HCl$ $+ 0.x\ (CH_3)_2CHCH(CH_3)CH_2O_2$ $+ 0.y\ (CH_3)_2CHC(O_2)(CH_3)_2$	2.1×10^{-10}	0
1035) $Cl + C_5H_{12} \rightarrow HCl + C_5H_{11}O_2$	2.5×10^{-10}	0

1036) $Cl + C_6H_{14}$ --> $HCl + C_6H_{13}O_2$	3.0×10^{-10}	0
1037) $Cl + C_7H_{16}$ --> $HCl + C_7H_{15}O_2$	3.4×10^{-10}	0
1038) $Cl + C_8H_{18}$ --> $HCl + C_8H_{17}O_2$	3.8×10^{-10}	0
1039) $Cl + CH_2O$ --> $HCl + HO_2 + CO$	7.3×10^{-11}	0
1040) $Cl + CH_3CHO$ --> $HCl + CH_3COO_2$	7.3×10^{-11}?	0
1041) $Cl + C_2H_5CHO$ --> $HCl +$ $C_2H_5COO_2$	7.3×10^{-11}?	0
1042) $Cl + i\text{-}C_3H_7CHO$ --> $HCl +$ $i\text{-}C_3H_7COO_2$	7.3×10^{-11}?	0
1043) $Cl + n\text{-}C_3H_7CHO$ --> $HCl +$ $n\text{-}C_3H_7COO_2$	7.3×10^{-11}?	0
1044) $Cl + n\text{-}C_4H_9CHO$ --> $HCl +$ $n\text{-}C_4H_9COO_2$	7.3×10^{-11}?	?
1045) $Cl + CH_2{=}CH_2$ (+M) --> $ClC_2H_4O_2$	1.1×10^{-10}	?
1046) $Cl + CH_3CH{=}CH_2$ (+M) --> $ClC_3H_6O_2$	2.4×10^{-10}	?
1047) $Cl + CO$ (+M) --> $ClCOO_2$	?	?
1048) $ClCOO_2 + NO$ --> $Cl + CO_2 + NO_2$	7.6×10^{-12}	-1.8×10^2
1049) $Cl + H_2O_2$ --> $HCl + HO_2$	3.9×10^{-13}	9.8×10^2
1050) $Cl + CH_3O_2H$ --> $HCl + CH_3O_2$	4×10^{-13}?	9.8×10^2?
1051) $ClC_2H_4O_2 + NO$ --> $ClCH_2CHO +$ $NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^2
1052) $ClC_3H_6O_2 + NO$ --> $ClCH_2COCH_3$ $+ NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^2

1053) $Cl + CH_3CH{=}CHCH_3$ --> $CH_3CH(Cl)CH(O_2)CH_3$	2.5×10^{-10}?	?
1054) $CH_3CH(Cl)CH(O_2)CH_3 + NO$ --> $CH_3CH(Cl)CH(O)CH_3 + NO_2$	7.6×10^{-12}	-1.8×10^{2}
1055) $CH_3CH(Cl)CH(O)CH_3 + O_2$ --> $CH_3CH(Cl)COCH_3 + HO_2$	2.2×10^{-14}	1.2×10^{2}
1056) $CH_3CH(Cl)CH(O)CH_3$ --> $CH_3CH(Cl)(O_2) + CH_3CHO$	1.8×10^{3}	7.5×10^{3}
1057) $CH_3CH(Cl)(O_2) + NO$ --> NO_2 $CH_3COCl + HO_2$	7.6×10^{-12}	-1.8×10^{2}
1058) $(CH_3)_2C{=}CH_2 + Cl$ --> $(CH_3)_2C(O_2)CH_2Cl$	2.4×10^{-10}	?
1059) $(CH_3)_2C(O_2)CH_2Cl + NO$ --> $(CH_3)_2C(O)CH_2Cl + NO_2$	7.6×10^{-12}	-1.8×10^{2}
1060) $(CH_3)_2C(O)CH_2Cl$ -->CH_3COCH_3 + $CH_2(Cl)(O_2)$	3.5×10^{3}	8.0×10^{3}
1061) $CH_2(Cl)(O_2) + NO$ --> $HC(Cl)O$ $NO_2 + HO_2$	7.6×10^{-12}	-1.8×10^{2}
1062) $HCl + HO$ --> $H_2O + Cl$	4.6×10^{-12}	5.0×10^{2}
1063) $Cl + O_2$ (+M) --> ClOO	4.9×10^{-14}	?
1064) ClOO (+M) --> $Cl + O_2$	9.2×10^{6}	3.0×10^{3}

APPENDIX B

THE ADMP CHEMISTRY ADVISORY GROUP

APPENDIX B

The ADMP Chemistry Advisory Group

Professor Roger Atkinson, University of California, Riverside, CA; Statewide Air Pollution Research Center.

Professor William Chameides, School of Geophysical Sciences, Georgia Institute of Technology, Atlanta, GA.

Professor Michael R. Hoffmann, Environmental Engineering Science, California Institute of Technology, Pasadena, CA.

Dr. Jennifer Logan, Chairperson of Chemistry Advisory Group of ADMP, Center for Earth Planetary Physics, Harvard University, Cambridge, MA.

Professor John Seinfeld, Department of Chemical Engineering, California Institute of Technology, Pasadena, CA.

Dr. Gary Whitten, Systems Applications Inc., San Raphael, CA.

Members of Other ADMP Advisory Groups Who Also Contribute to the Discussions of the Chemistry Advisory Panel

Professor Gregory Carmichael, Chemical and Material Engineering, University of Iowa, Iowa City, Iowa.

Professor Robert Carr, Department of Chemical Engineering & Material Science, University of Minnesota, Twin Cities, Minneapolis, Minn.

Dr. Thomas Graedel, Bell Laboratories, Murray Hill, NJ.

Dr. Robert Lamb, Environmental Sciences Research Laboratory, Research Triangle Park, NC.

Professor Gregory McRae, Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA.

Dr. Richard Stolarski, NASA/Goddard Space Flight Center, Greenbelt, MD.